

Synthesis and characterisation of 1,2-dihetarylethenes containing chlorobenzothiophene moieties

Mikhail M. Krayushkin,^{a*} Vasily A. Migulin,^{a,†} Vladimir N. Yarovenko,^a Valerii A. Barachevskii,^b Ludmila G. Vorontsova,^a Zoya A. Starikova,^c Igor V. Zavarzin^a and Valeriya N. Bulgakova^a

^a N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 137 6939; e-mail: mkray@ioc.ac.ru

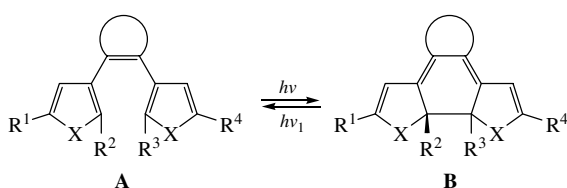
^b Photochemistry Center, Russian Academy of Sciences, 119421 Moscow, Russian Federation. E-mail: barva@photonics.ru

^c A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 135 5085

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Two novel 1,2-dihetarylethenes containing 5-chloro-2-methylbenzo[*b*]thiophene units and either cyclopentene or perfluorocyclopentene bridges were synthesised. Both compounds display photochromic properties in toluene solution; however, no photochromism was observed in the crystalline phase.

1,2-Dihetarylethenes are promising components for optoelectronics due to their unique ability to undergo a reversible interconversion under irradiation from an open (**A**) form to a cyclic (**B**) form.^{1,2}



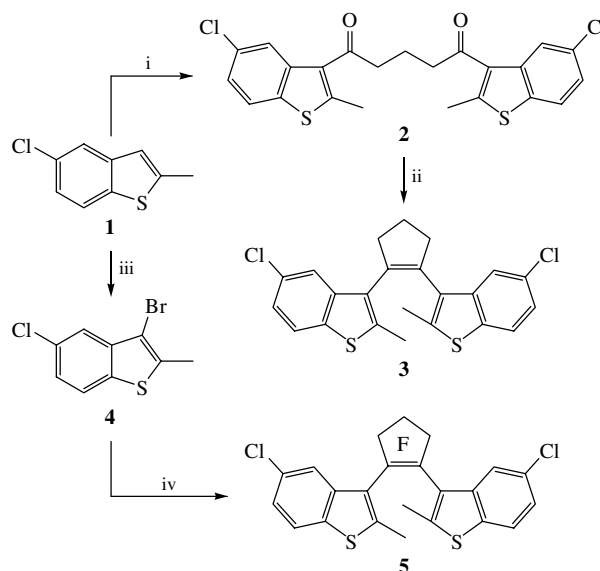
Photochromes containing benzothiophenes connected *via* a perfluorocyclopentene bridge show high fatigue resistance and thermal stability.¹ Analogous compounds with a cyclopentene bridge are much less studied; however, they also display attractive photochromic properties.³

The development of photo-operated photochromic polymers on the basis of dihetarylethenes with functional groups^{4,5} remains an appealing and promising field in organic and material chemistry.

Here, the synthesis of two novel photochromic dihetaryl-ethenes **3** and **5** containing 5-chloro-2-methylbenzo[*b*]thiophene fragments is described. New compounds have a potential to be independently utilised as photosensitive components of optical memory devices, and they could also serve as useful building blocks in the synthesis of various monomers.

Both 1,2-bis(5-chloro-2-methylbenzo[*b*]thiophen-3-yl)cyclopentene **3** and 1,2-bis(5-chloro-2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene **5** were synthesised starting from 5-chloro-2-methylbenzo[*b*]thiophene **1**.⁶ Diketone **2** was prepared by the slow addition of AlCl₃ (1.2 equiv.) to a solution of **1** (2 equiv.) and glutaryl chloride (1 equiv.) in CH₂Cl₂ cooled to –5 °C in 87% yield. Desired 1,2-dihetarylethene **3**[‡] was obtained by the McMurry coupling⁷ of diketone **2** using the Zn/TiCl₄ system in THF in 53% (Scheme 1).

3-Bromo-5-chloro-2-methylbenzothiophene **4** was prepared in 95% yield by the bromination of **1** in CHCl₃. Further lithiation



Scheme 1 Reagents and conditions: i, glutaryl chloride, AlCl₃, CH₂Cl₂, –5 °C; ii, TiCl₄, Zn, THF, 30 h, reflux; iii, Br₂, CHCl₃, –5 °C; iv, BuLi, perfluorocyclopentene, THF, –70 °C.

of **4** at a low temperature and the subsequent coupling with perfluorocyclopentene⁸ provided **5**[‡] in 43% yield after chromatography.

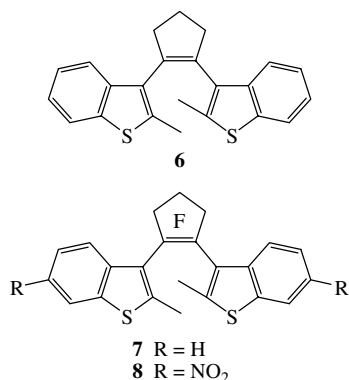
The utilization of a benzothiophene fragment with the fixed position of the halogen substituent in the aromatic ring pre-

[‡] ¹H and ¹³C NMR spectra were recorded in CDCl₃ solutions on Bruker WM-250 (250 MHz) and Bruker AC-200 (50 MHz) spectrometers, respectively. Chemical shifts were measured with reference to the carbons and residual protons of CDCl₃.

For **3**: mp 181–183 °C. ¹H NMR δ: 2.0–2.2 (br. s, 6H), 2.3 (t, 2H), 2.8–3.2 (br. m, 4H), 7.1–7.2 (m, 2H), 7.5–7.6 (m, 4H). ¹³C NMR δ: 14.98, 23.85, 29.59, 37.49, 121.73, 122.69, 123.56, 129.50, 129.99, 136.08, 136.77, 138.12, 140.23.

For **5**: mp 163–165 °C. ¹H NMR δ: 2.4 (s, 3H), 2.5 (s, 3H), 7.1–7.3 (m, 2H), 7.5–7.6 (m, 4H). ¹³C NMR δ: 15.31, 15.53, 116.06, 121.42, 121.68, 122.90, 123.16, 125.00, 125.11, 131.14, 131.54, 136.11, 136.41, 139.31, 144.46, 145.05, 157.06.

[†] A former student of the Higher Chemical College of the RAS (1992–1996).



determines the structure of final compounds **3** and **5**, which is an obvious advantage of the above approach. Our earlier attempts to synthesise **3** and **5** by the chlorination of known 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)cyclopentene **6**³ and 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene **7**⁹ led to the formation of inseparable multicomponent mixtures.

As expected, compounds **3** and **5** displayed photochromic properties in solution (toluene) (Table 1), which are similar to those of earlier synthesised dihetarylethenes.^{10,11}

Table 1 Photochemical characteristics of the synthesised 1,2-dihetarylethenes.^a

Compound	Initial form				Photoinduced form			
	λ_A/nm	D_A	λ_A^f/nm	I_A^f	λ_B/nm	ΔD_B^{max}	λ_B^f/nm	I_B^f
3	296	0.58	410	55.5	460	0.17	570	4.3
5	310	0.54	428	63	540	0.12	649	1.01

^a λ_A, λ_B are the absorption maxima wavelengths of the open (**A**) and cyclic (**B**) forms, respectively; λ_A^f, λ_B^f are the fluorescence maxima wavelengths of the open (**A**) and cyclic (**B**) forms, respectively; I_A^f, I_B^f are the comparative fluorescence intensities of the open (**A**) and cyclic (**B**) forms, respectively; D_A is the optical density at the absorption maxima of the open form (**A**); ΔD_B^{max} is the photoinduced change of the absorption maxima of the cyclic form (**B**).

A significant bathochromic shift of the absorption maximum of the cyclic form (by 80 nm) and a minor bathochromic shift of the absorption maximum of the open form (by 10–18 nm), which were observed by changing the cyclopentene bridge to the perfluorocyclopentene fragment in the molecule, are worth noticing. It could be concluded that only the open form is luminescent, since the fluorescence of the photoexcited cyclic form is characterised by a rather low intensity.[§]

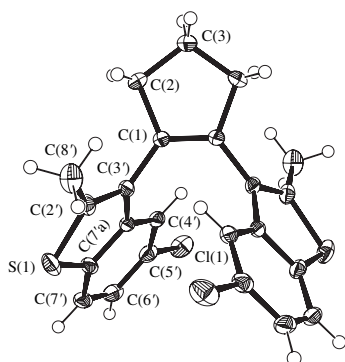


Figure 1 X-ray structure of **3**.

[§] Absorption spectra were measured in toluene solutions (4×10^{-4} M) in 2 mm thick quartz cells with a one-beam CARY UV 50 spectrophotometer (Varian). Fluorescence spectra were recorded in toluene solutions (8×10^{-5} M) in 1 cm thick cells using a CARY ECLIPSE spectrofluorimeter (Varian). Photochemical studies were performed with UV radiation of a DRSh-250 mercury lamp with $\lambda = 313$ nm with light filters and visible light radiation of the same lamp applying light filters of 546 and 436 nm.

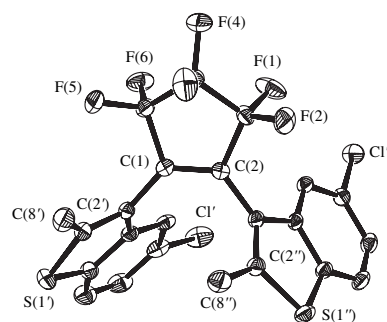


Figure 2 X-ray structure of **5a**.

Unexpectedly, neither **3** nor **5** showed photochromism in a crystalline phase, as compared with structurally similar 1,2-bis-(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene **8**.¹² To investigate this phenomenon, we studied the crystal structures of both **3** and **5** using X-ray analysis.

The molecule of **3** (Figure 1)[†] has 2₁ symmetry and occupies a special position on the two-fold axis of the unit cell. The cyclopentene bridge is planar. The dihedral angles between a cyclopentene plane and benzothiophene rings are 58.6° with an *anti*-parallel orientation of the latter. Thus, benzothiophene planes form a dihedral angle of 71.7°. However, due to their rotation in opposite directions over the C(1)–C(3') [C(1*)–C(3'*)] bonds the distances between the potentially reactive C(2')...C(2'*) centers reach a value of 5.358 Å, which considerably exceeds the allowed limit (~4.2 Å) for such a photocyclization to proceed.¹³ As a result, compound **3** remains inactive under irradiation in the crystalline state despite the *anti*-parallel conformation of the benzothiophene rings in the molecule. The similar picture was observed for **7** in a crystalline phase.¹²

The unit cell of a crystal of **5** includes two symmetrically independent molecules (**a** and **b**); the structure and the conformation of one of them (**a**) is shown in Figure 2. The comparison of geometrical and conformational parameters of **a** and **b** did not reveal any critical differences.[†] All bond lengths and bond angles correspond to the standard values.¹⁴ The perfluorocyclopentene fragment adopts an envelope conformation with the C(4) atom being deviated from the plane of other

[†] Crystallographic data for **3**: C₂₃H₁₈S₂Cl₂, $M = 429.39$, at 100 K, crystals are rhombic, space group *Ccc*₂, $a = 15.603(4)$, $b = 15.652(4)$ and $c = 8.229(2)$ Å, $V = 2009.5(8)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.419$ g cm⁻³.

Crystallographic data for **5**: C₂₃H₁₂S₂Cl₂F₆, $M = 537.35$, at 100 K, crystals are monoclinic, space group *P2*₁/*c*, $a = 21.413(5)$, $b = 13.184(3)$ and $c = 17.511(4)$ Å, $\beta = 113.81(4)^\circ$, $V = 4522.5(7)$ Å³, $Z = 8$, $d_{\text{calc}} = 1.578$ g cm⁻³.

The unit cell parameters and intensities of reflections were measured on a Bruker diffractometer [MoK α , graphite monochromator, ω -scan mode in the $1.84 \geq \theta \geq 30.0$ (**3**) and $1.04 \geq \theta \leq 28.0$ (**5**) ranges]. The structures were solved by the direct method, which revealed all non-hydrogen atoms, and refined by full-matrix least-squares in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were objectively revealed by difference electron density synthesis and refined isotropically by least-squares calculations. The final *R*-factors for 2774 (**3**) and 8906 (**5**) reflections with $I > 2\sigma(I)$ were $R_1 = 0.026$ (**3**), 0.042 (**5**), $wR_2 = 0.069$ (**3**), 0.087 (**5**). For all independent 2917 (**3**), 10712 (**5**) reflections $R_1 = 0.029$ (**3**), 0.054 (**5**), $wR_2 = 0.072$ (**3**), 0.097 (**5**). The calculations were performed using the APEX2¹⁶ and SHELXTL ver. 5.1¹⁷ program packages.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 629157 (**3**) and 629158 (**5**). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2007.

four cyclopentene carbons by 0.408 Å. The dihedral angles between the perfluorocyclopentene plane and each benzothiophene ring are 65.8° and 68.0°, while two benzothiophene planes form a dihedral angle of 72.7°. The parallel orientation of benzothiophene fragments in the crystal lattice is worth noting. It is known that, at such a conformation, any photocyclization is symmetrically prohibited.¹⁵ Thus, compound **5** in the crystalline state remains photochemically inactive. An analogous observation was reported for crystals of **8** obtained from an acetone solution.¹²

The obtained results should be considered while performing the synthesis of polymers based on **3** and **5** as monomers: it is possible that polymeric products could show no photochromic properties in the solid state.

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