ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 11, pp. 2088–2094. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.I. Tolmachev, V.V. Kurdyukov, Yu.G. Vlasenko, A.N. Chernega, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 11, pp. 1896–1902.

Synthesis, Molecular, and Crystal Structure of 3,4-Bis[(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl]cyclobut-3-ene-1,2-dione and -1,2-Dithione

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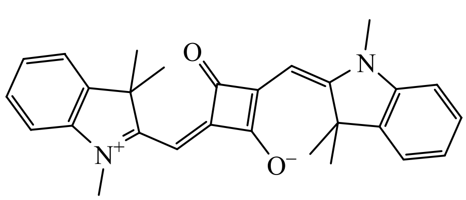
Received December 13, 2012

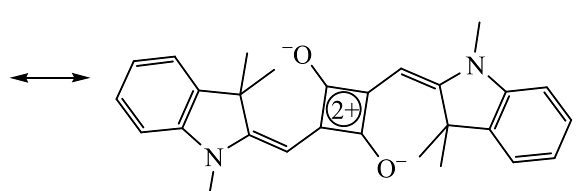
Abstract—Two new dyes have been prepared, 3,4-bis[(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl]-cyclobut-3-ene-1,2-dione and -1,2-dithione. Their molecular and crystal structures have been studied by X-ray diffraction, and their spectral properties have been characterized. The heterocyclic fragments in the dyes molecules are in the trans-position with respect to the bonds connecting chromophore CH group with the 4-membered ring. Substitution of the carbonyl oxygen to sulfur leads to change in the crystal packing.

DOI: 10.1134/S1070363213110224

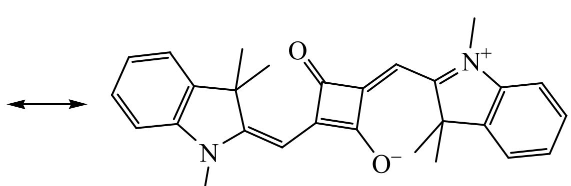
The organic dyes with chromophore containing cyclobutene fragment with two oxygen substituents (C_4O_2) can exist in the form of different isomers: the oxygen atoms can be either located at the neighbor carbon atoms, or in the β-position with respect to each other; the same applies to the electron-donor hetarylmethylidene or aromatic end groups. The both types of the dyes were first prepared more than 40 years ago [1]. Dyes of the second type, so called squaraine dyes, are well studied and widely applied [2, 3]. The methods of squaraine dyes preparation have been developed, their chemical and spectral properties have been investigated, and their electronic and spatial structures have been elucidated. Similarly to those of cyanine type, squaraine dyes contain the odd number of methine groups linking two electron-donor (hetero)aromatic fragments. One of those fragments is positively charged, whereas the other, conjugated with it, bears a lonely electron pair (**I**); therefore such dyes are sometimes referred to as cyanines. However, in the squaraine dyes the charge transfer of the donor–acceptor–donor type is observed (**Ib**) [2], which distinguishes then from the classical cyanine dyes.



Ia



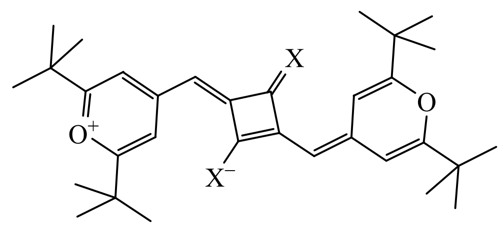
Ib



Ic

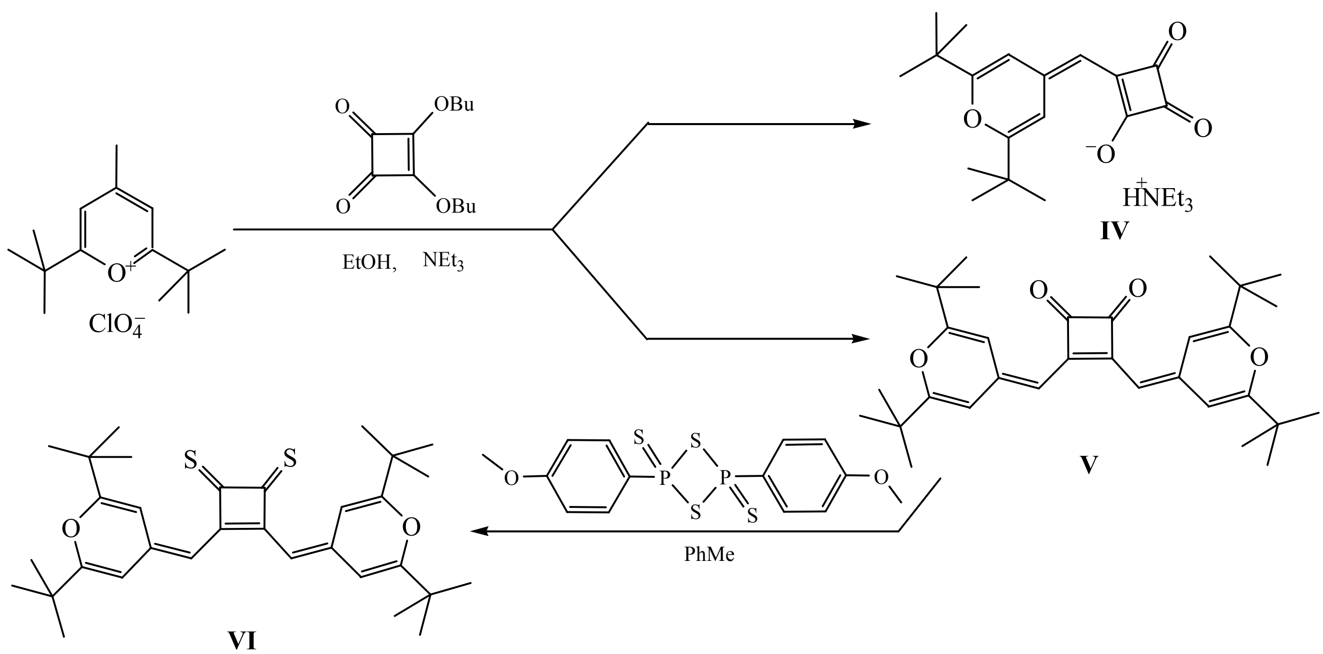
In contrast to the squaraine dyes, their 1,2-isomers have been less studied so far, being references in several publications only. In the pioneering work [1] such dyes (derivatives of pyridine, quinoline, and benzthiazole) were prepared by heating diethyl squarate with quaternary salts of methyl-substituted heterocycles in butanol in the presence of sodium butylate, and absorbance spectra of the products were studied. Later, preparation, oxidation, and spectral properties of 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclobutenedione have been described [4]. According to [5], 1,2-bis(4-dimethylaminophenyl)cyclobutene-3,4-dione has been isolated with 10% yield in the course of preparation of bis(4-dimethylaminophenyl)squaraine from dibutyl squarate and dimethylaniline in the water-saturated butanol with sulfuric acid, after the acidic filtrate was diluted with ether. Finally, in the review paper [3] it was suggested that the synthesis of squaraine dyes occurred in two stages. Firstly, the products of 1 : 1 condensation of squaric acid and the nucleophile were formed (the so called semisquaraines). Semisquaraines interaction with the second mole of the nucleophile could be not completely regioselective: the 1,2-isomer could be formed along with the product of 1,3-condensation. Due to higher solubility of the 1,2-product in the organic solvents, it was usually left in the solution after isolation of the 1,3-isomer.

The preparation and detailed studies of the isomers of squaraine dyes with carbonyl groups at the neighbor carbons of the cyclobutene ring are of unquestionable importance. Previously, we described the squaraine dye **II**, containing the 2,6-di-*tert*-butyl-4-pyrane fragments, as well as its dithio-substituted analog **III**; their electronic absorbance spectra [6, 7], molecular, and crystal structure [8] were studied.



II, X = O; **III**, X = S.

In this work we aimed to develop the method to prepare the 1,2-isomer of squaraine dye and its dithio analog (**V**, **VI**), and to study their spectral properties and molecular and crystal structure.



V was prepared along with the triethylammonium semisquaraine salt **IV** via condensation of 2,6-di-*tert*-butyl-4-methylpyrilium perchlorate with dibutyl squarate in ethanol in the presence of triethylamine.

The products were isolated by sequential chromatography, first on silica gel (eluent: benzene–chloroform 1 : 1) and then on aluminum oxide; at the latter stage, **V** and **IV** were eluted by dichloromethane

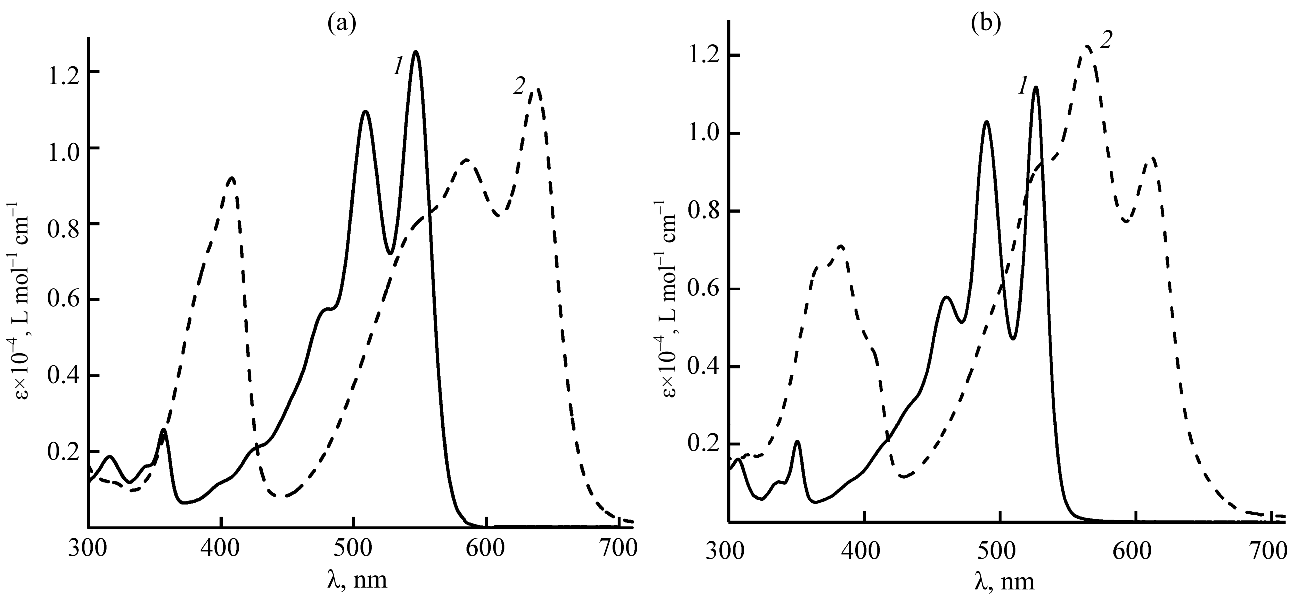


Fig. 1. Absorption spectra of the dyes (*1*) **V** and (*2*) **VI** in (a) dichloromethane and (b) *n*-hexane.

by ethanol–water–triethylamine 50 : 45 : 5, respectively. Dithiosquarate **VI** was prepared via reaction of **V** with the Lawesson's reagent.

In the electronic spectra of **V** and **VI**, as compared with those of the isomers **II** and **III** (Table 1), the absorption of the 1,2-derivatives was weaker and shifted towards shorter wavelength. The absorption spectra of prepared dyes contained two broad structured bands (Fig. 1). In the case of dithio-derivative **VI**, the short-wavelength band was more intense than that in the case of **V**. Similarly to the case of squaraine dyes **II** and **III**, the long-wavelength band of dithione **VI** was weaker and more diffuse than that of **V**.

Table 1. Spectral parameters of the dyes **II, III, V**, and **VI** [λ_{max}, nm (ε×10^{-4}, L mol^{-1} cm^{-1}]

Comp. no.	CH_2Cl_2	n-C_6H_{14}
II	346 (0.90), 645 (4.13), 713 (29.94)	372 (1.21), 649 (5.32), 719 (27.58)
III	449 (4.47), 750 (5.04)	412 (4.47), 486 (4.87), 811 (5.11)
V	316 (0.92), 357 (1.27), 479 (2.81), 509 (5.38), 547 (6.14)	352 (1.73), 460 (4.67), 490 (8.20), 526 (8.79)
VI	408 (4.63), 553 (4.11), 585 (4.86), 637 (5.83)	383 (2.76), 563 (4.91), 610 (3.68)

We also determined the λ_{max} of the long-wavelength bands of **II**, **III**, **V**, and **VI** in other solvents (Table 2) of different polarity. The polarity was characterized by the parameter $E_T(30)$ (kcal mol^{-1}), that equaled 31.0 and 40.7 in the cases of *n*-hexane and methylene chloride, respectively.

Similarly to the indolenine derivatives [10], in the case of pyrilium β-dione **II** we observed linear negative solvatochromism. Thiosquaraine **III** revealed sharper negative solvatochromism in the lower range of $E_T(30)$. In the cases of the isomeric 1,2-derivatives **V** and **VI**, weak positive solvatochromism was observed.

Evidently, the spectral properties of the dyes reflected their spatial molecular structure. In **II** and **III**, the heterocyclic fragments were in *trans*-orientation with respect to the 4-membered cycle; the narrow intense near-IR bands and weak short-wavelength bands were assigned to two chromophores, cationic and anionic, in their structures. According to ^{1}H NMR data on **V** and **VI**, their heterocyclic fragments were located in the *trans*-position with respect to the bonds linking the chromophore methine groups with the 4-membered ring.

^{1}H NMR spectra of **V** and **VI** were similar, containing the signals of *tert*-butyl groups, chain protons, and pyrane fragments. Noteworthily, the chemical shift of $H^{3,3'}$, located near oxygen of sulfur atoms of (thio)carbonyl groups, significantly differed from the signals of $H^{5,5'}$ in the pyrane ring (by 1.92 and 1.97 ppm in **V** and **VI**, respectively). In **VI**, the $H^{3,3'}$ signal was broadened, probably due to its stronger shielding by larger sulfur atom as compared to oxygen in **V**.

The bond lengths in isolated molecules of **V** and **VI** were computed by the non-empiric DFT/G6-31(d,p)/B3LYP method [11].

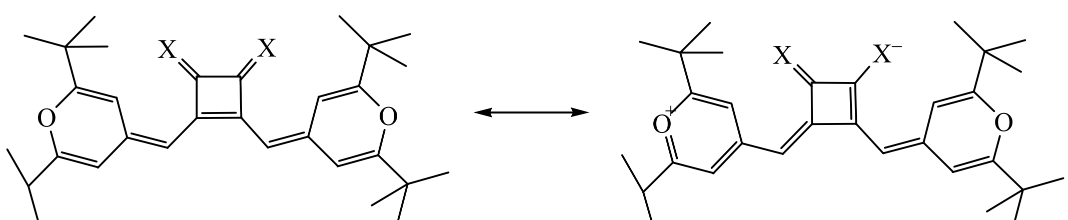
The features of molecular and crystal structures of those dyes as revealed by monocrystal X-ray diffraction are presented in Figs. 2 and 3. The 4-membered ring was almost planar in the both molecules, the deviation from planarity being more in the case of **VI**, due to larger 3,4-sulfur atoms. The highest deviation of the ring atoms from the plane was of 0.004 Å (**V**) and 0.023 Å (**VI**). The pyrane cycles were almost planar in the both molecules, the mean deviation of the positions of $C^{6–10}O^4$, $C^{12–16}O^3$ (**V**), $C^{6–10}O^1$, and $C^{20–24}O^2$ (**VI**) from the respective planes being less than 0.001 Å. Due to bulky 3,4-substituents, the rings $C^{6–10}O^4$ and $C^{12–16}O^3$ in **V** formed the dihedral angle of 18.23°. In **VI**, the dihedral angle between $C^{6–10}O^1$ and $C^{20–24}O^2$ planes was of 1.02°. The so pronounced difference was due to different location of

Table 2. Long-wavelength absorption maxima of **II, III, V**, and **VI** in the solvents of varied polarity

Solvent	$E_T(30)$, kcal mol^{-1}	λ_{max}, nm			
		II	**III**	**V**	**VI**
Toluene	33.9	725	785	539	629
Chloroform	39.1	714	752	546	637
N-Methylpyrrolidone	42.2	723	762	549	640
Ethanol	51.9	701	738	548	633
Methanol	55.4	698	738	548	633

(thio)carbonyl groups. In **V**, the O^1 and O^2 atoms were located practically in the plane of 4-membered ring (the deviations being of 0.003 Å, O^1 and 0.037 Å, O^2). On the contrary, in **VI** the sulfur atoms were significantly out of the ring plane (by 0.189 Å, S^1 and 0.145 Å, S^2, the torsion angle $S^1C^1C^2S^2$ was of 10.5°), thus allowing the pyrane substituents to accommodate in parallel.

The conformations of molecules of **V** and **VI**, as deduced from ^{1}H NMR and X-ray diffraction data, could be represented by mesomeric structures **A** and **B**.



A **B**

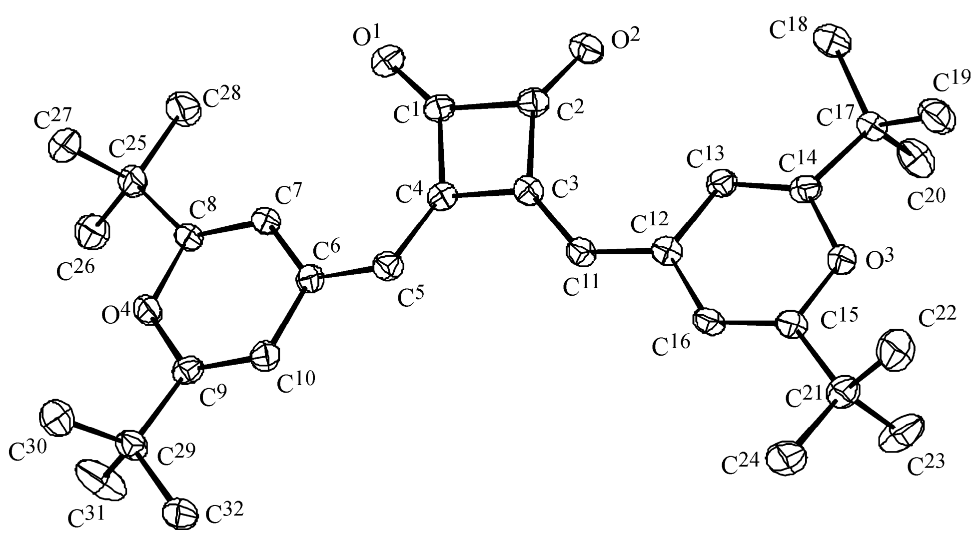


Fig. 2. General view of molecule of **V**.

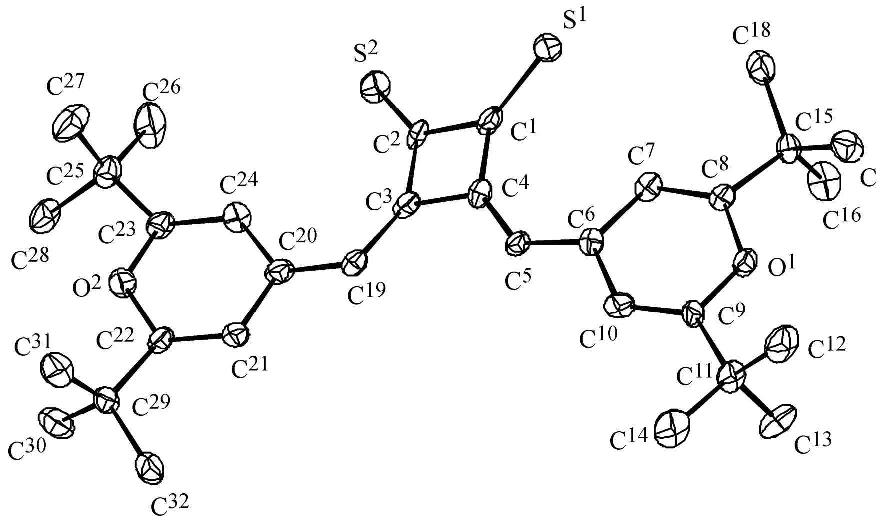


Fig. 3. General view of molecule of **VI**.

Table 3 lists the bond lengths in the conjugation chains of the prepared dyes, the experimental and theoretical values almost coincided. The shortest bond was C^6–C^5 one, pointing that the dyes **V** and **VI** should be regarded as bismerocyanines with crossing chromophores. Their weak positive solvatochromism was due to dominance of the nonpolar structure A. The C^6–C^5 bond was somewhat longer in the case of thione **VI**, likely due spacial distortion of the 4-membered ring and, thus, weaker conjugation.

In the crystal, parallel molecules of **V** were united into pairs forming a herringbone packing; in the case of **VI**, the molecules were organized in stacks (Figs. 4 and 5). Evidently, the different packing was due to interactions of the end heterocyclic groups. In the case of **V**, the positively charged end groups could efficiently interact with the negatively charged oxygen atom of the central fragment. In the case of **VI**, such interaction with sulfur atoms should have been less efficient. The similar effect of oxygen substitution with sulfur on the crystal packing was observed in the case of indoleine [12].

Table 3. Bond lengths (d, Å) in the conjugation chain of **V** and **VI**

Bond	V	VI
C^6–C^5	1.384[a] (1.368)[b]	1.390 (1.378)
C^5–C^4	1.415 (1.412)	1.409 (1.423)
C^4–C^1	1.491 (1.490)	1.472 (1.470)
C^4–C^3	1.420 (1.410)	1.442 (1.450)
C^1–O^1 (S^1)	1.218 (1.210)	1.665 (1.640)
C^1–C^2	1.597 (1.529)	1.394 (1.490)

[a] Computed. [b] XRD experiment.

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$ with Varian VXR-300 spectrometer (299.9 MHz, TMS as internal standard). Electronic absorption spectra were registered with Shimadzu UV-3100 spectrophotometer, (l = 1 cm, c = 10^{-5} mol/L). TLC was performed with Silufol UV-254 plates with benzene–chloroform 2 : 1 as eluent. Column chromatography was preformed with silica gel (70–230 μm, Merck) and aluminum oxide 90.

Triethylammonium 2-[(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl]-3,4-dioxocyclobut-1-ene-1-olate (IV) and 3,4-bis-[(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl]cyclobut-3-ene-1,2-dione (V). 0.202 g (2 mmol) of triethylamine was added to a stirred mixture of 0.613 g (2 mmol) of 2,6-di-*tert*-butyl-4-methylpyrilium perchlorate and 0.226 g (1 mmol) of dibutyl squarate in 25 mL of ethanol at 75°C. The mixture was incubated during 10 min, then cooled down, and stripped under reduced pressure. The residue was separated by silica gel chromatography with benzene–chloroform. Red-orange fraction was further purified by Al_2O_3 chromatography with dichloromethane. The product was crystallized from acetonitrile. Yield of **V** 0.147 g (30%), mp 240–242°C. ^{1}H NMR spectrum, δ, ppm: 1.24 s (18H, *t*-Bu), 1.28 s (18H, *t*-Bu), 5.46 s (2H, CH), 5.97 s (2H, β-H), 7.89 s (2H, β'-H). Found, %: C 78.47; H 8.50. $C_{32}H_{42}O_4$. Calculated, %: C 78.33; H 8.63.

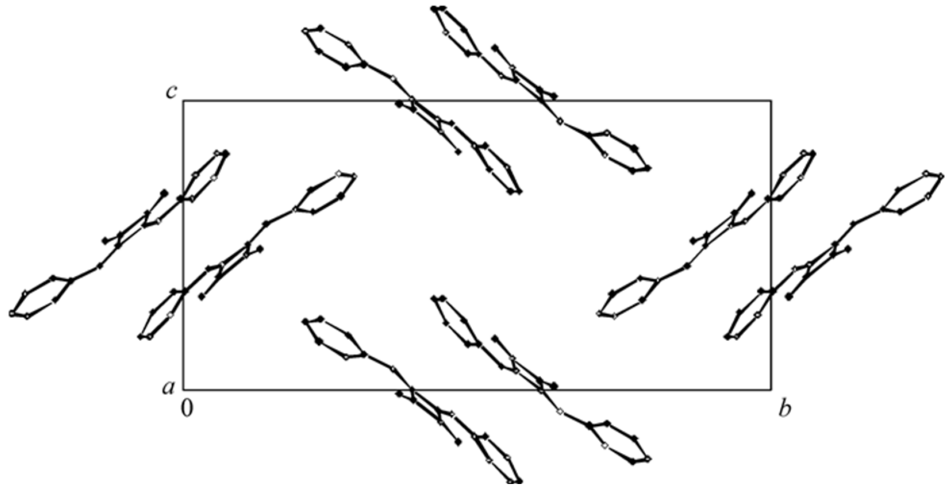


Fig. 4. Crystal packing of **V**.

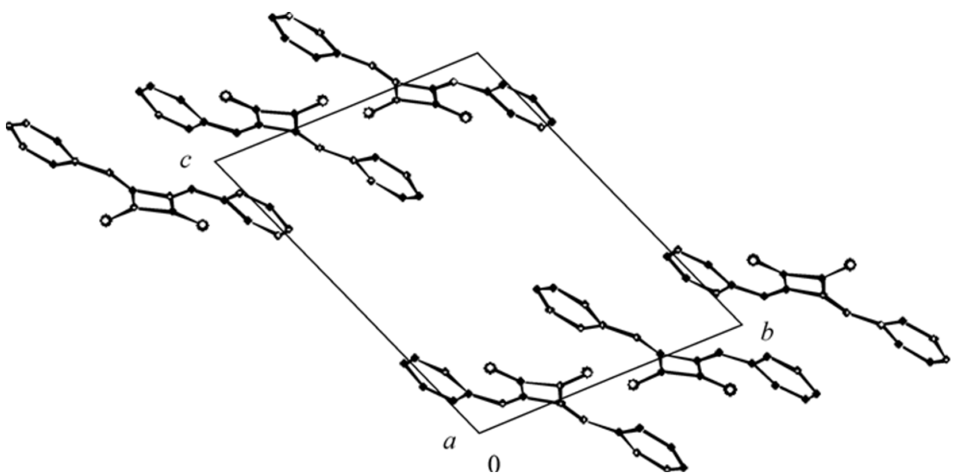


Fig. 5. Crystal packing of **VI**.

The yellow fraction was eluted from Al_2O_3 with ethanol–water–triethylamine 50 : 45 : 5. The solvents were evaporated under reduced pressure; the residue was dissolved in dichloromethane, filtered, and stripped. The product **IV** was crystallized from acetonitrile–water 5 : 1. Yield 0.195 g (48%), mp 134–135°C. ^{1}H NMR spectrum, δ, ppm: 1.14 s (9H, *t*-Bu), 1.17 s (9H, *t*-Bu), 1.17 t (3H, Me, *J* 7.5 Hz), 3.05–3.16 m (6H, NCH_2), 5.34 s (1H, CH), 5.79 d (1H, β-H, *J* 1.5 Hz), 7.69 d (1H, β'-H, *J* 1.5 Hz), 9.01 br. s (1H, NH). UV spectrum (EtOH), λ_{max}, nm ($\varepsilon\times10^{-4}$): 252 (1.26), 282 (0.96), 426 (3.64). Found, %: C 71.17; H 9.20; N 3.40. $C_{24}H_{37}NO_4$. Calculated, %: C 71.43; H 9.24; N 3.47.

3,4-Bis-[(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)methyl]cyclobut-3-ene-1,2-dithione (VI). 0.490 g (1.2 mmol) of the Lawesson's reagent was added to a solution of 0.490 g (1 mmol) of **V** in 50 mL of anhydrous toluene under argon. The mixture was incubated during 30 min at 100°C. After cooling down, the product was isolated by silica gel chromatography with toluene and crystallized from acetonitrile. Yield 0.230 g (44%), mp 220–222°C. ^{1}H NMR spectrum, δ, ppm: 1.27 s (36H, *t*-Bu); 5.68 s (2H, CH); 6.23 s (2H, β-H), 8.19 br. s (2H, β'-H). Found, %: C 73.37; H 8.02; S 12.12. $C_{32}H_{42}O_2S_2$. Calculated, %: C 73.52; H 8.10; S 12.27.

X-Ray diffraction analysis. Dyes crystals for XRD study were grown from acetonitrile solutions. The XRD study was performed at –100°C with Bruker Apex **II** automated CCD-diffractometer (MoK_α, λ = 0.71069 Å). In total, 33636 (**V**) and 10807 (**VI**) reflections were registered; 5883 (**V**) and 4852 (**VI**) of them were independent [R_{int} 0.057 (**V**) and 0.066 (**VI**)] and used in the further adjustment. The structures were solved via direct method and adjusted via least squares method in the full matrix anisotropic approximation using the CRYSTALS software package [13]. 2290 reflections with $I > 3\sigma(I)$ (7.05 reflections per parameter) (**V**) and 1556 reflections with $I > 2\sigma(I)$ (4.79 reflections per parameter) (**VI**) were used ащк adjustment. All hydrogen atoms were located from the differential synthesis of electron density and included into the adjustment with the fixed position and thermal parameters. The final divergence factors were of R_w 0.034, R_1 0.032, and GOF 1.156 (**V**); R_w 0.062, R_1 0.072, and GOF 1.146 (**VI**).

Crystals of V ($C_{32}H_{42}O_4$, *M* 490.68) were monoclinic, space group $P2_1/c$ (no. 14), cell parameters at 173 K: *a* 10.1503(3), *b* 24.2765(8), *c* 12.8156(4) A, β 110.546(2)°, **V** 2957.1(2) A^3, *Z* 4, d_{calc} 1.10 g cm^{-3}, $\mu(MoK_\alpha)$ 0.071 mm^{-1}, *F*(000) 1064.

Crystals of VI ($C_{32}H_{42}O_2S_2$, *M* 522.82) were triclinic, space group *P*-1 (no. 2), cell parameters at 173 K: *a* 10.398(3), *b* 10.867(4), *c* 14.955(4) A, α 107.956(7), β 106.864(7), γ 99.11(1)°, **V** 1480.2(8) A^3, *Z* 2, d_{calc} 1.17 g cm^{-3}, $\mu(MoK_\alpha)$ 0.206 mm^{-1}, *F*(000) 564.

The XRD data were deposited to the Cambridge Crystallographic Data Center [CCDC 800277 (**V**), CCDC 800278 (**VI**)].

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