Dyes and Pigments 79 (2008) 242–246

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A novel synthetic route to thiacyanine dyes containing a perfluorinated polymethine chain

L.M. Yagupolskii*, N.V. Kondratenko, O.I. Chernega, A.N. Chernega, S.A. Buth, Yu.L. Yagupolskii

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, 02094 Murmanskaya street 5, Kiev-94 02094, Ukraine

ARTICLE INFO

Article history:
Received 25 December 2007
Received in revised form 12 March 2008
Accepted 13 March 2008
Available online 20 March 2008

Keywords:
2-Trifluorovinylbenzothiazole
Fluoride ion
Thiacarbocyanine dye
Perfluorinated polymethine chain
α,β-Difluorosubstituted dyes

ABSTRACT

2-Iodobenzothiazole was reacted with tributyl(trifluorovinyl)tin and (2-chlorodifluorovinyl)tributyltin by the Stille reaction to yield 2-trifluorovinyl- and 2-(2-chlorodifluorovinyl)benzothiazole, respectively. The quaternary salt of 2-trifluorovinylbenzothiazole, when treated with fluoride ion, furnished the corresponding thiacarbocyanine dye containing a perfluorinated polymethine chain. The reaction involved nontrivial cleavage of the C–C bond to provide an energetically advantageous conjugated perfluoropolyenic system.

1. Introduction

Organic molecules containing a perfluorinated conjugated chain (F-chromophore) belong to the family of artifacts created by fluorine chemistry. Such systems are classified with two types, both synthesized and investigated by our research group [1–5]. These are perfluoropolyenes (mainly α,ω-diaryl substituted molecules such as Ar-(CF=CF)$_n$-Ar, $n = 2$–6) and cyanine dyes with the perfluorinated chain, the latter being limited to the only example of thiacarbocyanine. In the course of these studies, we established a significant possibility of transmitting electronic effects through the perfluorinated conjugated chain. A surprising and remarkable fact was also revealed: the fluorine atom, the most electronegative one, influences absorption maxima like an electron-donor substituent. Thus, according to the Foerster–Dewar–Knott rule, the absorption maximum is significantly shifted to longer wavelengths by fluorine atoms at the α- and γ-positions of the polymethine chain and to shorter wavelengths by fluorine atoms at the β-position [6,7], just as is the case with typical electron-donor groups.

2. Results and discussion

Though the dyes with the perfluorinated trimethine and longer conjugated chains show much promise, e.g., in colour theory of organic compounds and in nonlinear optics, the methods to synthesize them have yet to be developed.

Such dyes can be obtained starting from 2-trifluorovinyl- and 2-(2-chlorodifluorovinyl)-substituted benzothiazoles **1** and **2**. The former compound was obtained previously by the condensation of *o*-aminothiophenol and tetrafluorosuccinic anhydride followed by the decarboxylation of sodium benzothiazolyl-2-tetrafluoropropionate [8]. An alternative synthetic route to **1** implies condensation of 2-iodobenzothiazole with labile trifluorovinylzinc chloride [4]. Benzothiazole derivative **2** was obtained by the condensation of 2-benzothiazolyllithium with chlorotrifluoroethylene [9]. However, stable yields of compounds **1** and **2** are afforded by none of these methods.

We have developed a novel synthetic route to the compounds of this kind that involves the Stille reaction of 2-iodobenzothiazole with tributyl(trifluorovinyl)tin **3** and (2-chlorodifluorovinyl)tributyltin **4** [10].

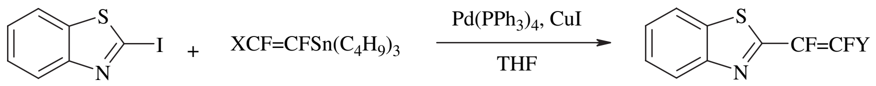
Trifluorovinyltin derivative **3** was synthesized by the procedure [11] and its properties completely agree with the literature data [12,13]; to the best of our knowledge, there is no evidence about chlorodifluorovinyl analogue **4** in the literature. Tin derivatives **3** and **4** are stable for heating and storage.

The previously described [4] thiacarbocyanine **7** containing the perfluorinated polymethine chain and *N*-methyl groups was obtained on reacting 2-(2-chlorodifluorovinyl)benzothiazolium tetrafluoroborate with 2-fluoromethylbenzothiazolium tetrafluoroborate in the presence of *p*-diethylaminotoluene. In order to perform X-ray diffraction analysis, we also prepared analogous *N*-ethyl-substituted dye **8** using the same scheme (Scheme 1).

---

* Corresponding author.
E-mail address: yagupolskii@ioch.kiev.ua (L.M. Yagupolskii).

0143-7208/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2008.03.003



X = F **3**, Cl **4**.

Y = F **1**, Cl **2**

A disadvantage of this method is that the quaternary salts of 2-fluoromethylbenzothiazole are prepared using high toxic reagents, namely monofluoroacetic acid derivatives [14].

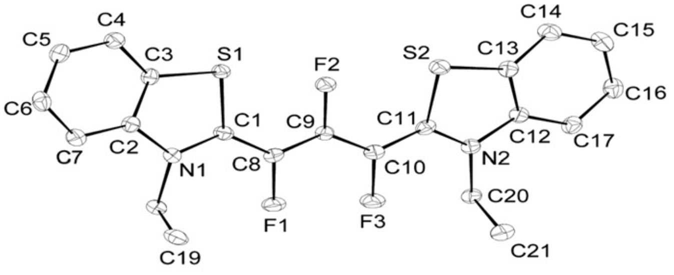
Another method to obtain dye **7** containing *N*-methyl groups was previously described by one of us based on the self-condensation of *N*-methyl-2-trifluorovinylbenzothiazolium tetrafluoroborate in the presence of *N*,*N*-diethylaniline [3]. This approach, however, does not provide stable results.

Here we describe a new access to cyanine dye **7** which implies self-condensation of the quaternary salt of 2-trifluorovinylbenzothiazole **9** in the presence of the fluoride ion. It should be noted that the nature of the cation in the fluoride salt is of great significance. Thus, tetramethylammonium fluoride in a nitromethane solution causes an immediate colour change and the reaction is completed within some minutes, whereas the usage of CsF requires 2–3 h and KF – 8–9 h to reach the key product. In all cases, a fluoride salt was added to the quaternary salt in the 1:2 molar ratio. The reaction proceeds by Scheme 1.

We assume that the addition of the fluoride ion to salt **9** occurs on the first stage, followed by the resulting anion attack to another molecule **9** and, finally, elimination of CF_4 led to dye **7**. This rather uncommon cleavage of the strong C–C bond is justified by the formation of an energetically preferable conjugated perfluorinated system.

The structure of dyes **7** and **8** has been determined by the X-ray diffraction method. The bond lengths and angles in the perfluorinated chain are virtually the same as in the polymethine chain of the corresponding thiacarbocyanine 3-ethyl-2-[3-(3-ethyl-2,3-dihydrobenzothiazolyliden-2)-propenyl]benzothiazolium tetrafluoroborate **10** [15,16].

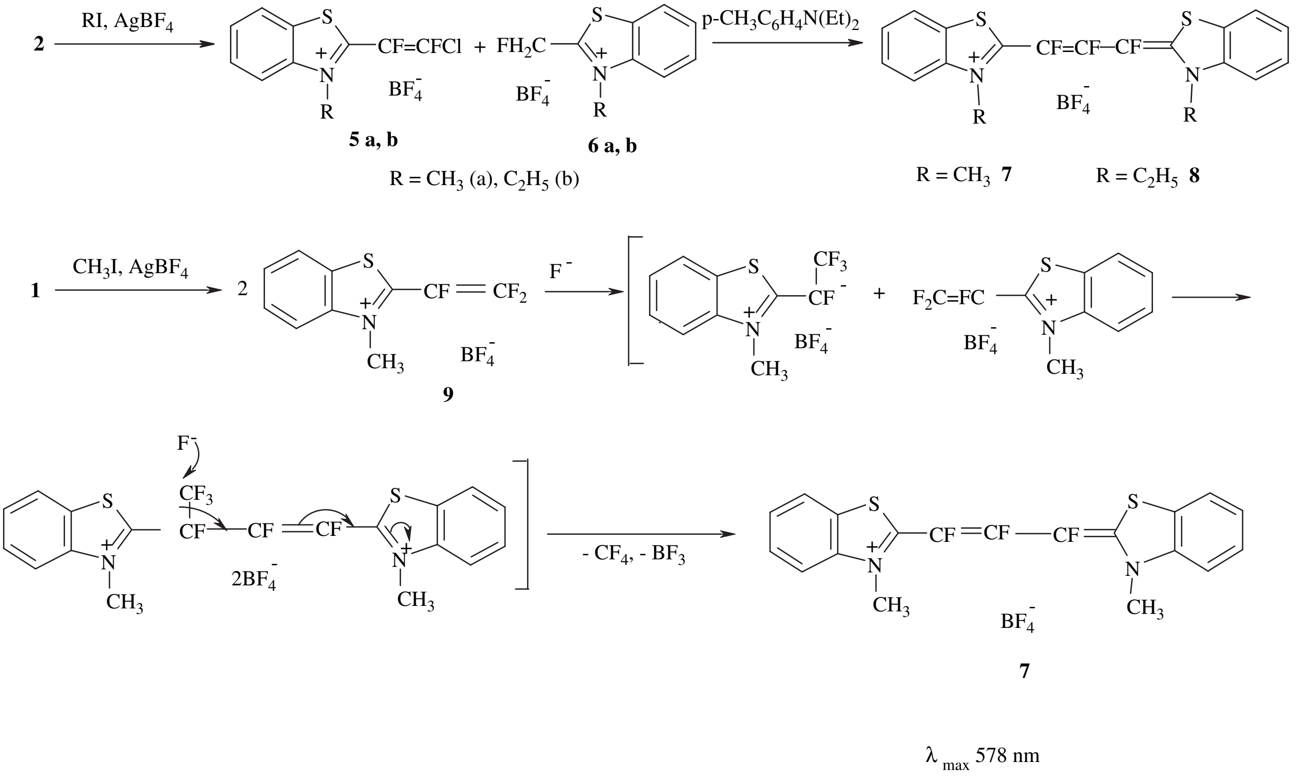
In both compounds, the cations are approximately planar: the deviations from the least-square plane do not exceed 0.29 Å for **7** and 0.13 Å for **8**; the dihedral angle between the fragments C(1–7)N(1)S(1) and C(11–17)N(2)S(2) is 10.96° for **7** and 7.17° for **8**; the torsion angles S(1)C(1)C(8)C(9), S(2)C(11)C(10)C(9), C(1)C(8)C(9)C(10), C(8)C(9)C(10)C(11) are 9.13°, 5.59°, 4.05°, 0.16° for **7** and 6.10°, 8.56°, 3.24°, 2.65° for **8**, respectively.



*The molecular structure of dye **8***

The following table summarizes bond lengths in the polymethine chain of dyes **7**, **8**, and **10**

Dye no.	*N*-alkyl	Conjugated chain C_8–C_{10}	C_1–C_8	C_8–C_9	C_9–C_{10}	C_{10}–C_{11}
7	$-CH_3$	–CF=CF–CF=	1.401(5)	1.376(5)	1.393(5)	1.392(5)
8	$-C_2H_5$	–CF=CF–CF=	1.399(3)	1.384(3)	1.378(4)	1.411(3)
10	$-C_2H_5$	–CH=CH–CH=	1.391(4)	1.383(4)	1.384(4)	1.393(4)



Scheme 1.

The transmission of electronic effects through the perfluorinated conjugated chain is demonstrated well by the absorption maximum value of benzothiacarbocyanine **7** with the perfluorinated chromophore (λ_{max} 578 nm) which is 20 nm shifted to red as compared to its unsubstituted counterpart **10** and has much the same intensity (cf. ε 13.75 × 10^4 l/(mol cm) for **7** and 14.00 × 10^4 l/(mol cm) for **10**) [8]. The bathochromic shift of the fluorinated dye absorption maximum value results from the fact that two fluorine atoms at the α,γ-positions of the trimethine chain exert a larger effect as electron-donors than one fluorine atom at the β-position.

The spectral effect of fluorine atoms in the polymethine chain has also been studied in α,β-disubstituted dyes series. The quaternary salt of benzothiazole **5a** was condensed with julolidine to give cationic dye **11** and with malononitrile to give neutral merocyanine **12** (Scheme 2).

The absorption maxima of dyes **11** and **12**, and the previously obtained styryl dye [14], all containing the perfluorinated dimethine chain, are very close to, or even coincide with their unsubstituted analogues (cf. λ_{max} 565 and 572 nm [17], 449 and 446 nm [18], 530 and 530 nm [14], the first values referring to fluorine-containing dyes). The very slight effect of fluorine substitution in this case is due to a mutual cancellation of the red shift caused by the α-fluorine atom and the blue shift caused by the β-fluorine atom [14].

To conclude, we have found facile synthetic routes to benzothiazole derivatives containing unsaturated fluorinated groups in the 2-position and obtained the corresponding polymethine dyes on their basis. The methods developed are applicable in the synthesis of other perfluoroalkenyl substituted heterocycles and cyanines with the perfluorinated polymethine chain.

3. Experimental

All reactions were carried out under dry argon in annealed glassware using freshly distilled solvents such as pentane (dried over Na), THF (dried over Na/benzophenone), ether (double-distilled over $LiAlH_4$ and kept over CaH_2) acetonitrile (dried over P_2O_5 and CaH_2), nitromethane, dichloroethane (dried over P_2O_5 and freshly annealed K_2CO_3), chloroform (washed with a solution of K_2CO_3, dried over $MgSO_4$, and distilled over freshly annealed K_2CO_3). Fluoride salts ($(CH_3)_4NF$, CsF, and KF) were thoroughly vacuum-annealed before use. A 2.5 N solution of BuLi in hexane and Bu_3SnCl were provided by Aldrich and Acros, respectively. Single crystals of **7** and **8** were crystallized from nitromethane, mounted in inert oil, and transferred to the cold gas stream of the diffractometer.

Electronic absorption spectra were recorded on a spectrophotometer Specord M40. ^1H and 19F NMR spectra were recorded on a Varian VXR-300 in below mentioned solvents.

*3.1. 2-Trifluorovinylbenzothiazole (**1**)*

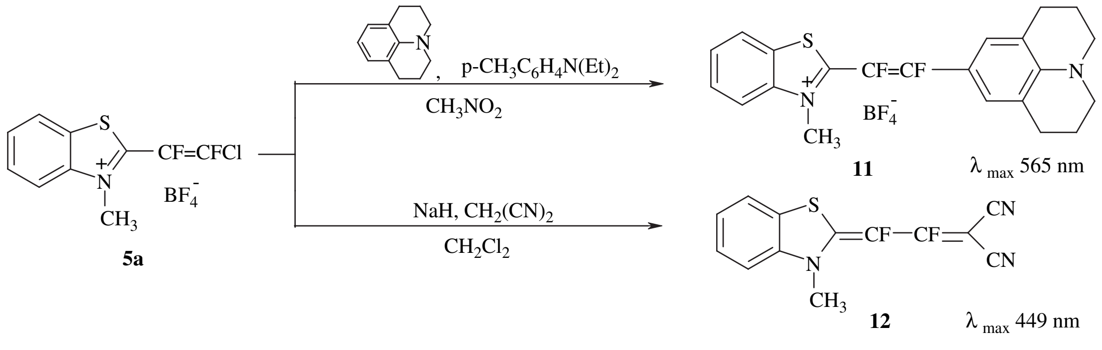
A mixture of 2-iodobenzothiazole [19] (2.6 g, 10 mmol), $Pd(PPh_3)_4$ (0.5 g, 4.3 mol%), CuI (1 g, 5 mmol), and tributyl(trifluorovinyl)tin **3** (4.1 g, 11 mmol) in THF (30 ml) was stirred at 50 °C for 24 h. The resulting precipitate was filtered off and THF was evaporated in vacuo at 30 °C. The mixture of compound **1** and Bu_3SnI was extracted from the residue with pentane (2 × 15 ml) and pentane was evaporated in vacuo at 20 °C. The residue was mixed with a KF (1.3 g) solution in 30% EtOH (10 ml). The precipitate of Bu_3SnF was filtered off and washed with ether (20 ml); **1** was extracted from the filtrate with ether (30 ml). The combined ether solution was washed with ice water (2 × 20 ml) and dried with $MgSO_4$ for 40 min. The ether was evaporated in vacuo at 20 °C and the residue was flash-chromatographed from pentane on a 10 × 1 cm column of silica gel. The first portion (10 ml) was discarded and the fraction of 60–70 ml was collected. Pentane was evaporated in vacuo at 20 °C. Compound **1** was obtained as pale-yellow crystals. A keeping time is no longer than 24 h at −10 °C. Yield: 1.37 g (64%); m.p. 57–58 °C. δ_H (299.5 MHz; $CDCl_3$; Me_4Si) 7.14–8.11 (4H, m, Ar); δ_F (188.1 MHz; $CDCl_3$; $CFCl_3$) −92.6 (1F, dd, $J = 40.5$ Hz, $J = 33.2$ Hz), −104.3 (1F, dd, $J = 112.0$ Hz, $J = 40.5$ Hz), −176.4 (1F, dd, $J = 112.0$ Hz, $J = 33.2$ Hz). Element analysis for $C_9H_4F_3NS$ Calc.: F, 26.51; found: F, 26.33%.

*3.2. (2-Chloro-1,2-difluorovinyl)tri(*n*-butyl)tin (**4**)*

To a stirred solution of ClCF=CFCl (17.29 g, 130 mmol) in ether (80 ml) and THF (80 ml), *n*-BuLi (40 ml, 2.5 N, 100 mmol) was added with a syringe over 1 h at −100 °C. The mixture was allowed to stand at this temperature for 1 h and then Bu_3SnCl (32.5 g, 100 mmol) was added with a syringe at −90 °C. After standing at this temperature for 1 h, the mixture was heated to −40 °C over 1 h, again held for 1 h, and then heated to room temperature over 1 h, followed by stirring for 10 h. The reaction mixture was poured onto ice (300 g), treated with ether (200 ml) and KF (20 g), and shaken. The ether layer was separated, washed with water (2 × 50 ml), and dried with $MgSO_4$. The solvent was evaporated and the residue was distilled, to give compound **4** as a colourless oil (*cis*:*trans* 30:70). Yield: 27 g (69.7%); b.p. 91–97 °C (0.5 mm Hg). n_D^{18} 1.4760. δ_H (299.5 MHz; $CDCl_3$; Me_4Si) 0.76–1.66 (27H, m, 3 × C_4H_9); δ_F (188.1 MHz; $CDCl_3$; $CFCl_3$) *cis* isomer: −88.0 (1F, d, $J = 12.4$ Hz), −136.9 (1F, d, $J = 12.4$ Hz); *trans* isomer: −123.0 (1F, d, $J = 127.7$ Hz), −153.4 (1F, d, $J = 127.7$ Hz). Element analysis for $C_{14}H_{27}ClF_2Sn$ Calc.: Cl, 9.16; found: Cl, 8.86%.

*3.3. 2-(2-Chloro-1,2-difluorovinyl)benzothiazole (**2**)*

It was synthesized analogously to compound **1** (the reaction reached completion within 72 h). To separate compound **2** from the



Scheme 2.

oil formed on extraction with pentane, the fraction with boiling point under 120 °C (0.2 mm Hg) was collected and chromatographed on silica gel with the mixture hexane:ethyl acetate (10:1) used as eluent. Product **2** was isolated as a *cis–trans* isomer mixture. On recrystallization from hexane, the *trans* isomer was obtained. Yield: 1.2 g (52%); m.p. 113–114 °C. δ_H (299.5 MHz; $CDCl_3$; Me_4Si) 7.43–8.15 (4H, m, Ar); δ_F (188.1 MHz; $CDCl_3$; $CFCl_3$) *cis* isomer: −92.4 (1F, d, $J = 11.7$ Hz), −135.6 (1F, d, $J = 11.7$ Hz); *trans* isomer: −106.3 (1F, d, $J = 125.5$ Hz), −149.2 (1F, d, $J = 125.5$ Hz). Element analysis for $C_9H_4ClF_2NS$ Calc.: C, 46.65; H, 1.72; Cl, 15.33; found: C, 46.70; H, 1.75; Cl 15.4%.

*3.4. Tetrafluoroborates of 2-(2-chloro-1,2-difluorovinyl)-3-methylbenzothiazolium (**5a**), 2-(2-chloro-1,2-difluorovinyl)-3-ethylbenzothiazolium (**5b**) and 3-methyl-2-(1,2,2-trifluorovinyl)benzothiazolium (**9**)*

To an ice-cooled solution of base **1** (0.86 g, 4 mmol) or **2** (0.926 g, 4 mmol) and an appropriate alkyl iodide (12 mmol) in dichloroethane (20 ml), $AgBF_4$ (1.1 g, 5.6 mmol) was added as a single portion. After stirring the mixture at room temperature for 24 h, dichloroethane was evaporated in vacuo at 30 °C, and the residue was dried in vacuo (0.5 mm Hg) for 1 h. Then nitromethane (7 ml) was added and AgI was filtered off. The filtrate was concentrated in vacuo to a volume of 2–2.5 ml, and the quaternary salt was precipitated with anhydrous ether (20 ml). The solvent was decanted and the salt was again recrystallized from CH_3NO_2 (2 ml) with ether (10 ml). After decanting the solvent, the salt was dried in vacuo (0.5 mm Hg) at 30 °C for 4 h.

Yield of product **5a**: 0.81 g (60.6%); m.p. 216–218 °C (dec). δ_H (299.5 MHz; CD_3COCD_3; Me_4Si) 4.7 (3H, s, CH_3), 8.01–8.67 (4H, m, Ar); δ_F (188.1 MHz; CD_3COCD_3; $CFCl_3$) *trans*: −92.5 (1F, d, $J = 129.8$ Hz), −144.3 (1F, d, $J = 129.8$ Hz), −150.5 (4F, s, BF_4). Element analysis for $C_{10}H_7BClF_6NS$ Calc.: F, 34.18; found: F, 34.25%.

Yield of product **5b**: 0.76 g (54.5%); m.p. 130 °C (dec). δ_H (299.5 MHz; CD_3COCD_3; Me_4Si) 1.8 (3H, t, $J = 7.3$ Hz, CH_3) 5.18 (2H, m, CH_2), 7.58–8.67 (4H, m, Ar); δ_F (188.1 MHz; CH_3NO_2; $CFCl_3$) −91.2 (1F, d, $J = 129.9$ Hz), −147.0 (1F, d, $J = 129.9$ Hz), −151.8 (4F, s, BF_4). Element analysis for $C_{11}H_9BClF_6NS$ Calc.: C, 37.98; H, 2.58; found: C, 36.69; H, 2.30%.

Yield of product **9**: 0.73 g (57.9%); m.p. 130–132 °C (dec). δ_F (188.1 MHz; CH_3NO_2; $CFCl_3$) −87.1 (1F, dd, $J = 40.6$ Hz, $J = 31.5$ Hz), −101.2 (1F, dd, $J = 115.8$ Hz, $J = 40.6$ Hz), −150.9 (4F,s, BF_4), −168.2 (1F, dd, $J = 115.8$ Hz, $J = 31.5$ Hz). Element analysis for $C_{10}H_7BF_7NS$ Calc.: C, 37.85; H, 2.20; found: C, 37.31; H, 2.58%.

*3.5. 3-Methyl-2-[3-(3-methyl-2,3-dihydrobenzothiazolyliden-2)-1,2,3-trifluoropropenyl]benzothiazolium tetrafluoroborate (**7**)*

A solution of **9** (0.1 g, 0.31 mmol) in CH_3CN (2 ml) and anhydrous CsF (0.024 g, 0.15 mmol) were stirred for 3 h at room temperature. Compound **7** was precipitated with anhydrous ether (15 ml) and purified by chromatographing on silica gel. After washing away an impurity of $CHCl_3$, **7** was eluted with the mixture $CHCl_3$:CH_3NO_2 (10:4). Yield: 0.05 g (30%); m.p. 225–227 °C (dec). λ_{max} (CH_3CN)/nm 578; ε 13.75×10^4 l/(mol cm) in CH_3CN. δ_H (299.5 MHz; DMSO; Me_4Si) 4.69 (6H, s, 2 × CH_3), 8.0–8.5 (8H, m, 2 × Ar); δ_F (188.1 MHz; DMSO) −130.0 (1F, t, $J = 85.8$ Hz, CF), −152.1 (4F, s, BF_4), −169.8 (2F, d, $J = 85.8$ Hz, 2 × CF); δ_C (125.76 MHz; DMSO; Me_4Si) 37.80 (t, ${}^4J_{CF} = 6.6$ Hz), 114.74 (s), 123.64 (s), 126.50 (s), 126.72 (d, ${}^4J_{CF} = 10.7$ Hz), 129.02 (s), 128.79 (2×dd, ${}^1J_{CF} = 232.5$ Hz, ${}^2J_{CF} = 37.0$ Hz, ${}^3J_{CF} = 8.6$ Hz), 142.20 (s), 153.43 (m), 154.05 (2×t, ${}^1J_{CF} = 245.5$ Hz, ${}^2J_{CF} = 32.7$ Hz). Element analysis for $C_{19}H_{14}BF_7N_2S_2$ Calc.: C, 47.69; H, 2.93; found: C, 47.69; H, 3.14%.

*3.5.1. Crystal structure determination of compound (**7**)*

Crystal data and data collection parameters. $[C_{19}H_{14}F_3N_2S_2]^+ \cdot [BF_4]^- \cdot CH_3NO_2$, $M = 539.30$, triclinic, $a = 6.9579(3)$, $b = 11.3770(5)$, $c = 15.0344(5)$ Å, $\alpha = 71.961(3)$, $\beta = 81.873(3)$, $\gamma = 76.195(3)°$, $V = 1096.00(8)$ Å^3, (by least-squares refinement on 1720 reflections, $3.0 \le \theta \le 25.7°$), $T = 173$ K, space group P-1, $Z = 2$, $D_c = 1.63$ Mg m^{-3}, $F(000) = 548$, violet needles with dimensions $0.80 \times 0.10 \times 0.09$, μ(Mo K_α) = 0.328 mm^{-1}, SADABS absorption correction (the ratio of minimum to maximum apparent transmission is 0.69); Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å), data collection range $1.9 \le \theta \le 26.5°$, $-8 \le h \le 8$, $-13 \le k \le 11$, $-16 \le l \le 18$; 6898 reflections measured, 4327 independent ($R_{int} = 0.02$), 2720 reflections ($I > 3.00\sigma(I)$) were used in calculations.

Structure solutions and refinement. The structure was solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by the full-matrix least-squares technique, on F (CRYSTALS program package) [20]. Hydrogen atoms were located in the difference Fourier maps and refined isotropically. The Chebyshev weighting scheme [21] was applied with parameters 1.44, 0.902, 1.06. The final $R = 0.046$ and $R_w = 0.053$, GOF = 1.108 for 384 parameters (obs/var ratio 7.08); $\Delta\rho_{min} = -0.48$ e Å^{-3}, $\Delta\rho_{max} = 0.66$ e Å^{-3}. CCDC 669465.

*3.6. 3-Ethyl-2-[3-(3-ethyl-2,3-dihydrobenzothiazolyliden-2)-1,2,3-trifluoropropenyl]benzothiazolium tetrafluoroborate (**8**)*

N-Ethyl-2-fluoromethylbenzothiazolium tetrafluoroborate [14] (0.142 g, 0.5 mmol) was mixed with *p*-diethylaminotoluene (0.163 g, 1 mmol) in CH_3NO_2 (2 ml) and added to a solution of salt **5b** (0.175 g, 0.5 mmol) in CH_3NO_2 (2 ml). After stirring for 10 min, dye **8** was precipitated with dry ether (20 ml). The solvent was decanted and product **8** was purified by chromatographing on silica gel using the mixture $CHCl_3$:CH_3NO_2 (20:6) as eluent. Yield: 0.16 g (79%); m.p. 205–208 °C (dec). λ_{max} (CH_3CN)/nm 578; ε 12.91×10^4 l/(mol cm) in CH_3CN. δ_H (299.5 MHz; DMSO; Me_4Si) 1.48 (6H, t, $J = 6.9$ Hz, 2 × CH_3), 4.58 (4H, q, $J = 7.2$ Hz, $J = 14.4$ Hz, 2 × CH_2), 7.50–8.14 (8H, m, 2 × C_6H_4); δ_F (188.1 MHz; DMSO) −132.3 (1F, t, $J = 84.0$ Hz, CF), −148.8 (4F, s, BF_4), −173.3 (2F, d, $J = 84.0$ Hz, 2 × CF); δ_C (125.7 MHz; DMSO; Me_4Si) 14.78 (s), 46.01 (t, ${}^4J_{CF} = 6.4$ Hz), 114.40 (s), 123.76 (s), 126.56 (s), 126.91 (d, ${}^4J_{CF} = 12.7$ Hz), 129.15 (s), 129.16 (2×dd ${}^1J_{CF} = 238.1$ Hz, ${}^2J_{CF} = 36.72$ Hz, ${}^3J_{CF} = 11.6$ Hz), 141.13 (s), 152.06 (m), 155.16 (2×t, ${}^1J_{CF} = 243.8$ Hz, ${}^2J_{CF} = 33.6$ Hz). Element analysis for $C_{21}H_{18}BF_7N_2S_2$ Calc.: C, 49.80; H, 3.55; found: C, 50.38; H, 3.71%.

*3.6.1. Crystal structure determination of compound (**8**)*

Crystal data and data collection parameters. $[C_{21}H_{18}F_3N_2S_2]^+ \cdot [BF_4]^- \cdot CH_3NO_2$, $M = 506.32$, triclinic, $a = 10.3748(2)$, $b = 10.6115(2)$, $c = 11.1250(2)$ Å, $\alpha = 105.897(2)$, $\beta = 93.336(2)$, $\gamma = 113.771(1)°$, $V = 1058.04(4)$ Å^3, (by least-squares refinement on 2872 reflections, $2.2 \le \theta \le 28.4°$), $T = 123$ K, space group P-1, $Z = 2$, $D_c = 1.59$ Mg m^{-3}, $F(000) = 516$, violet bricks with dimensions $0.38 \times 0.16 \times 0.13$, μ(Mo K_α) = 0.326 mm^{-1}, SADABS absorption correction (the ratio of minimum to maximum apparent transmission is 0.85); Bruker Smart Apex II CCD area-detector diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å), data collection range $1.9 \le \theta \le 28.5°$, $-12 \le h \le 13$, $-14 \le k \le 13$, $-14 \le l \le 14$; 9063 reflections measured, 4744 independent ($R_{int} = 0.02$), 3168 reflections ($I > 3.00\sigma(I)$) were used in calculations.

Structure solutions and refinement. The structure was solved by direct methods and subsequent Fourier difference techniques, and refined anisotropically, by the full-matrix least-squares technique, on F (CRYSTALS program package) [20]. Hydrogen atoms were located in the difference Fourier maps and refined isotropically. The

Chebyshev weighting scheme [21] was applied with parameters 0.607 0.360 0.304. The final $R = 0.038$ and $R_w = 0.043$, GOF = 1.129 for 366 parameters (obs/var ratio 8.66); $\Delta\rho_{min} = -0.42$ e Å^{-3}, $\Delta\rho_{max} = 0.58$ e Å^{-3}. CCDC 669464.

3.7. 2-{1,2-Difluoro-2-[2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinol-9-yl]vinyl}-3-methylbenzothiazolium tetrafluoroborate (**11**)

From a solution of salt **5a** (0.121 g, 0.36 mmol) and julolidine (0.124 g, 0.72 mmol) in CH_3NO_2 (2 ml) allowed to stand for 24 h, dye **11** was precipitated with ether (20 ml) and purified analogously to dye **12**. Yield: 0.13 g (77.4%); m.p. 201 °C (dec). λ_{max} (CH_3CN)/nm 563; ε 6.68×10^4 l/(mol cm) in CH_3CN. δ_H (299.5 MHz; CD_3COCD_3; Me_4Si) 2.01 (4H, m, $2 \times CH_2$), 2.8 (4H, m, $2 \times CH_2$), 3.5 (4H, t, $J = 5.8$ Hz, $2 \times CH_2$), 4.5 (3H, d, $J = 4.1$ Hz, CH_3), 7.5 (2H, s, $2 \times$ CH Ar), 7.7–8.3 (4H, m, Ar); δ_F (188.1 MHz; CD_3COCD_3; $CFCl_3$) −116.2 (1F, d, $J = 109.2$ Hz), −151.0 (4F, s, BF_4), −161.0 (1F, d, $J = 109.2$ Hz). Element analysis for $C_{22}H_{21}BF_6N_2S$ Calc.: C, 56.17; H, 4.46; found: C, 56.20; H, 4.37%.

3.8. 2-[1,2-Difluoro-2-(3-methyl-2,3-dihydrobenzothiazol-2-ylidene)ethylidene]malononitrile (**12**)

To a solution of $CH_2(CN)_2$ (0.099 g, 1.5 mmol) in anhydrous CH_2Cl_2 (20 ml), NaH (60%, 0.12 g, 3 mmol) was added; 30 min later, the mixture was cooled to −25 °C, followed by adding compound **5a** (0.5 g, 1.5 mmol) and stirring at this temperature for 1 h and at room temperature for 2 h. The resulting precipitate was filtered off and recrystallized from $CHCl_3$ to obtain merocyanine **12** (0.1 g). On chromatographing the mother solution in CH_2Cl_2 on silica gel, with the mixture $CHCl_3$:CH_3CN (10:1) used as eluent, another portion of dye **12** (0.07 g) was obtained. Yield: 0.17 g (41.46%); m.p. 275–278 °C (dec). λ_{max} (CH_3CN)/nm 449; ε 8.5×10^4 l/(mol cm) in CH_3CN. δ_H (299.5 MHz; DMSO; Me_4Si) 4.0 (3H, d, $J = 4.5$ Hz, CH_3), 7.4–8.0 (4H, m, Ar); δ_F (188.1 MHz; DMSO; $CFCl_3$) −106.4 (1F, d, $J = 91.7$ Hz, CF), −170.2 (1F, d, $J = 91.7$ Hz, CF). Element analysis for $C_{13}H_7F_2N_3S$ Calc.: C, 56.72; H, 2.54; found: C, 56.60; H, 2.55%.

References

[1] Yagupolskii LM, Kulchitskii MM, Ilchenko AY. Zh Org Khim 1972;8:2447.
[2] Yagupolskii LM, Ilchenko AY, Kulchitskii MM. Dokl AN SSSR 1973;209:138–40.
[3] Kulchitskii MM, Ilchenko AY, Yagupolskii LM. Zh Org Khim 1973;9:827–32.
[4] Yagupolskii LM, Yagupolskii YL. Zh Org Khim 1977;13:1996–2000.
[5] Kremlev MM, Yagupolskii LM. J Fluorine Chem 1998;91:109–23.
[6] Yagupolskii LM, Ilchenko AY, Gandelsman LZ. Usp Khim 1983;52:1732–59.
[7] Ilchenko AY, Yagupolskii LM. Ukr Khim Zh 2006;72:114–6.
[8] Yagupolskii LM, Malichenko NA. Zh Obshch Khim 1966;37:1798–802.
[9] Gillet JP, Sauvetre R, Normant JF. Synthesis 1986:538–43.
[10] Farina V, Krishnamurthy V, Scott WJ. In: Paquette Leo A, editor. Organic reactions, vol. 50. New York: John Wiley & Sons, Inc; 1997. p. 398.
[11] Raghavanpillai A, Burton DJ. J Org Chem 2004;69:7083–91.
[12] Xue L, Lu L, Pedersen SD, Liu Q, Narske RM, Burton DJ. J Org Chem 1997;62:1064–71.
[13] Seyferth D, Raab G, Brandle KA. J Org Chem 1961;26:2934–7.
[14] Yagupolskii LM, Gruz BE. Zh Obshch Khim 1967;37:2470–5.
[15] Von Allman, Anis H, Benn R, Grahn W, Olejnek S, Waskowska A. Angew Chem Suppl 1983:1147–75.
[16] Yagupolskii LM, Kondratenko NV, Chernega OI, Chernega AN, Buth SA, Yagupolskii Yu L. Molecular and crystal structure of 2-[3-(3-ethylbenzothiazolylidene-2)propenyl]-3-ethylbenzothiazolium tetrafluoroborate. Cambridge Crystallographic Data Centre, private communication, Dep. N. 669747; November 2007.
[17] Mikhailenko FA, Balina LV. Khim Geterotsikl Soedin 1982:450–2.
[18] Kulinich AV, Derevyanko NA, Ishchenko AA. Izv AN. Russ Chem Bull 2005;54:2820–30.
[19] Iversen PE. Acta Chem Scand 1968;22:1690–1.
[20] Watkin DJ, Prout CK, Carruthers JR, Betteridge PW. Crystals Issue 11. Oxford: Chemical Crystallography Laboratory, University of Oxford; 1996.
[21] Carruthers JR, Watkin DJ. Acta Crystallogr A 1979;35(N 3):698–9.