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Synthesis of the first representative of dicarbothiacyanine dyes with completely fluorinated polymethine chain

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ABSTRACT

2-Iodobenzothiazole was reacted with tributyl(pentafluorobutadienyl)tin in the Stille reaction conditions to give 2-pentafluorobutadienylbenzothiazole **1**. The quaternary salt of **1** via interaction with 2-fluoromethylbenzothiazole methylene base, obtained *in situ*, forms two cyanine dyes **8** and **9** as a result of nucleophilic attack of two different positions of perfluorobutadiene chain. The pure 2-fluoromethylbenzothiazole methylene base (in a dimer form) was obtained by deprotonation of the corresponding salt by NaH and on reacting with **1** forms the dye base **11** that underwent electrocyclization and subsequent HF addition to form the cyclohexadiene **12** identified by X-ray analysis data. Upon quaternization and HF abstraction by toluidine the recyclization occurred and dye **8** – the first representative of dicarbothiacyanine dyes with perfluorinated polymethine chain – was obtained. It has λ_{max} = 691 nm, that is 41 nm more than in non fluorinated dye, vinylene shift is equal to 111 nm.

1. Introduction

Cyanine dyes constitute one of the classical (since 1856) but still modern class of organic compounds due to their validated income to the basic problems of organic synthesis and physico-chemical investigations as well as numerous applications of them in modern technology [1]. Main structure of cyanine dyes is presented by a system of conjugate bonds with terminal groups that intensify colour (auxochromes). The income of fluorine chemistry to this field started in 1950 by pioneering investigations of Prof. Lev Yagupolskii and his co-workers in Kiev, Ukraine, with modification of heterocyclic rings by fluorine atom and fluorine containing substituents (that yielded in development of the practically applied imidacarbocyanine with SO_2CF_3 group as effective sensitizer for colour films) [2]. But the most intriguing problem to solve was the modification of polymethine conjugation chain by fluorine atoms as far as the possibility of electron effect transmission through it was not obvious.

Yagupolskii et al. have proved that there is a principal possibility that electron effects are transferred via perfluorinated conjugation chain [3,4]. This is revealed by p*K*a analysis of 1,2-difluorocinnamic and 5-arylperfluoropentadienic acids [5], dipole moments, UV and NMR ^{19}F spectra of E-α,β-difluorostilbene derivatives [6] and a number of dimethylaminopolyfluoromethine dyes with absorption maxima 120–150 nm deeper than those of the hydrocarbon analogs [7]. According to quantum-chemical calculations this equals to the influence of vinylene group in polymethine dyes [8].

The correlation between length of dye absorption wave and structural changes in polymethine chain was fixed in Förster, Dewar and Knott papers (the FDK rule) [9,10]. The rule states that at the uneven position of polymethine chain electron-donating groups provoke hypsochrome shift of the absorption band and electron-withdrawing substituents initiate the bathochrome shift, whereas the substituents at the even positions initiate the opposite shifts. Studying absorption spectra of thiacarbocyanines with fluorine atoms at different positions in chain Yagupolskii and his co-workers have encountered a remarkable fact: the most electronegative fluorine atom acts like an electron-donating substituent [2,11]. This is explained by the fact that substituents conjugation effect in the chain has stronger influence on dyes absorption spectrum than the induction effect [10–12].

It is noteworthy to mention that investigations in the field of fluorine containing cyanine dyes in the last decade were limited to the examples of symmetrical [13], unsymmetrical [14] and squaraine [15] thiacyanines that contained fluorine atoms or CF_3-group in the heterocyclic rings, whereas modification of

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polymethine chain still remains to the exclusive field of scientific research by Prof. Lev Yagupolskii and his group.

The cyanine dyes of benzothiazole are the most investigated organic dyes and basic rules of the colour theory that establish correlation between structure and absorption of dyes are results of investigations of thiacyanines. Recently we have presented a synthetic route to thiacarbocyanine dye that contains perfluorinated trimethine chain [16]. Introduction of three fluorine atoms in this case resulted into appreciable dye bathochromic colour shift.

Thiadicarbocyanine pentamethine chromophore is especially sensitive to the effect of the substituents, that is why the elongation of fluorinated chain in thiacyanine dyes and investigation of the influence of fluorine atoms on colour of fluorinated dicarbocyanine benzothiazole dye in comparison with hydrocarbon analogue is of particular interest. Dicarbocyanine dyes containing fluorine atoms at the α,ω [17] and β,γ,δ-positions of polymethine chain have been obtained by Yagupolskii et al., the last group of compounds has been synthesized via reaction of perfluoroalkyliodides with methylene base of corresponding heterocycles under UV light [18–20].

We now report studies on the synthesis of the first representative of dicarbothiacyanine dyes with completely fluorinated pentamethine chain and examination of its UV spectral peculiarities in comparison with non- and polyfluorinated analogs.

2. Results and discussion

The basic compound for synthesis of perfluoromethine dicarbocyanines of the benzothiazole series is 1-(2-benzothiazolyl)-pentafluoro-1,3-butadiene **1**. Few aromatic 1-arylpentafluoro-1,3-butadienes have been obtained via the interaction of arylmagnesium compounds and perfluoro-1,3-butadiene [21], to the best of our knowledge heterocyclic derivatives of such type are unknown. According to the procedure [22] we have synthesized benzothiazole-2-ylmagnesium chloride and introduced it into reaction with perfluoro-1,3-butadiene (Scheme 1).

Formation of benzothiazole **1** has been observed in the reaction mixture (according to ^{19}F NMR data) with 9–10% yield, but we failed to isolate the pure product.

Earlier we have synthesized 2-trifluorovinylbenzothiazole by the Stille reaction of 2-iodobenzothiazole and CF_2=$CFSnBu_3$ **2** [16], and we decided to use CF_2=CF–CF=CF–$SnBu_3$ in the same type of transformation. The *trans*-isomer of this compound was obtained by Burton and co-workers [23] from *trans*-CF_2=CF–CF=$CFSiEt_3$ **3** synthesized on reacting *trans*-ICF=CFSiEt$_3$ [24] and ICF=CF_2. We have obtained silane **3** via a more convenient method having replaced expensive and difficult-to-access ICF=CF_2 with CF_2=$CFSnBu_3$ (Scheme 2).

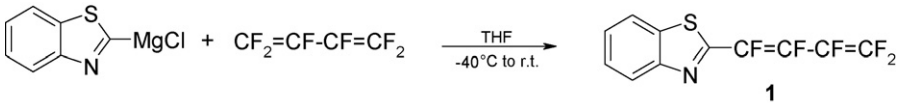
The preparation of stannane **2** was documented earlier in reactions of corresponding trifluorovinylmagnesium [25–28], -lithium [28] or silyle [23] reagents with Bu_3SnCl. The scheme of stannane **2** synthesis from easy-to-access F 134a (CF_3CHF_2), $LiNiPr_2$, and Bu_3SnCl at 15–20 °C is given in paper [29], but details of the procedure unfortunately are not described. According to our data under such conditions only decomposition of the product occurs and stannane **2** has been isolated on performing reaction at −78 °C to −80 °C with 85% yield.

Silane **3** has been transformed into CF_2=CF–CF=$CFSnBu_3$ **4** by the action of KF and Bu_3SnCl according to Ref. [23]. In addition to procedure [23] after chromatography from pentane the product was distillated in vacuum (b.p. 74–76 °C/0.1 mm Hg, n_D^{18} = 1.4611). Stannane **4** can be stored unchanged at −20 °C in Ar atmosphere for approximately 20 days.

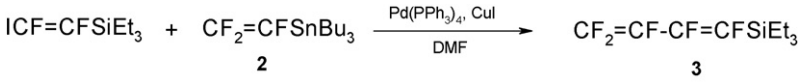
We have found that CF_2=CF–CF=$CFSnBu_3$ enters the Stille cross-coupling with 2-iodobenzothiazole in the presence of $Pd(PPh_3)_4$ and CuI to form 2-perfluorobutadienylbenzothiazole **1** with sufficient yield. Compound **1** as well as 2-trifluorovinylbenzothiazole is rather unstable, but after thorough purification by chromatography on silica gel compound **1** can be stored in Ar atmosphere at −20 °C for a long time.

The quaternary salt **5** has been synthesized via alkylation of benzothiazole **1** with CH_3I in the presence of $AgBF_4$ and was well preserved at −18 °C for sufficient period (Scheme 3).

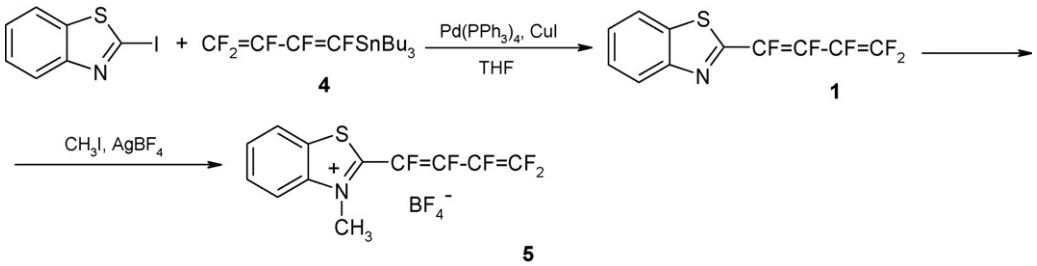
In order to obtain the key dye **8** we performed reaction of quaternary salt **5** and 2-fluoromethylbenzothiazole methylene base **7**, prepared *in situ* from 2-fluoromethyl-benzothiazolium tetrafluoroborate **6** and toluidine in DME. The UV spectroscopy data indicated formation of two dyes, one possessing λ_{max} = 691 nm, the other – 660 nm. Formation of two dyes may



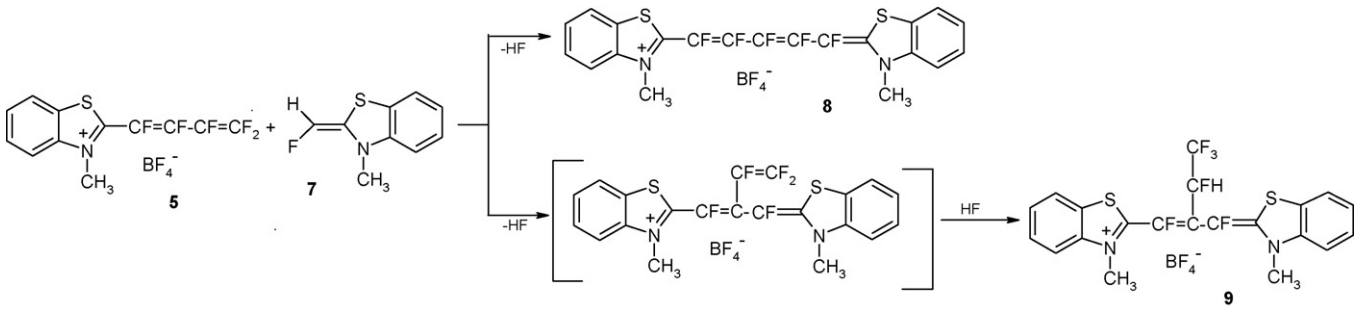
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

Scheme 5.

be explained as a result of nucleophile attack of two different perfluorobutadiene chain positions in the salt **5** – β-CF-group and terminal CF_2-group – both bearing partial positive charge due to the electron-withdrawing influence of the quaternary nitrogen atom of heterocycle. The condensation of terminal CF_2-group with methylene base leads to dicarbocyanine **8**, the reaction of β-CF-group yields carbocyanine **9** (Scheme 4).

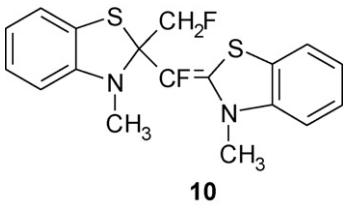
Dyes **8** and **9** are difficult to separate via chromatography, thus they have been isolated with low yields. Three groups of signals in 2:2:1 ratio have been fixed in dye **8** ^{19}F NMR spectrum which corresponds with dicarbocyanine pentafluoromethine chain. The ^{1}H NMR spectrum has only indicated signals of benzothiazole ring and $-CH_3$ groups. The dye **9** ^{19}F NMR spectrum has revealed signals in 3:2:1 ratio which corresponds with CF_3-group, CHF-group and two CF-groups of trimethine chain. The ^{1}H NMR spectrum has indicated signals of hydrogen atoms of benzothiazole rings, $-CH_3$ groups and a CHF group.

Attempts to obtain crystals from dyes **8** and **9** for X-ray diffraction analysis were unsuccessful, thus we have carried out an independent synthesis to verify dye **8** structure.

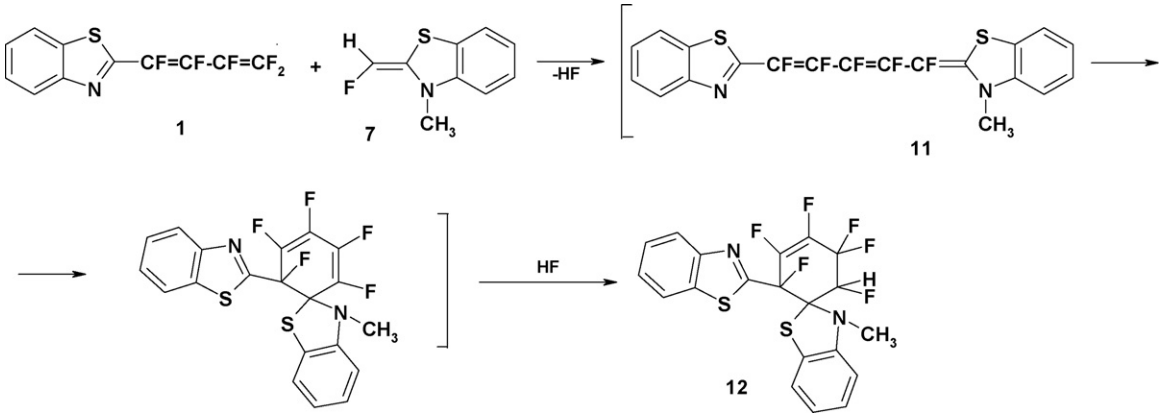
In contrast to salt **5** the partial positive charge in benzothiazole **1** perfluoromethine chain is located mainly on CF_2-group and we expected that this very position should undergo the fluoromethylene base **7** attack.

In publication [30] the isolated base **7** is described as viscous oil formed via NaH and NEt_3 interaction with 2-fluoromethyl-3-methylbenzothiazolium chloride in benzene solution. We have carried out this synthesis and have fixed ^{19}F NMR signals of fluorine atoms of methylene base dimer and ^{1}H NMR spectrum corresponds with its complex with NEt_3 in 1:20 ratio. The excess of NEt_3 is not removed even after prolonged drying of the complex in vacuum that raises necessity of pure methylene base synthesis. We have found that methylene base **7** can be obtained in pure form on reacting of salt **6** with NaH in DME solution (Scheme 5).

Cryoscopy and ^{1}H NMR spectroscopy data [31–34] have proved that the nonfluorinated methylene base synthesized from 2,3-dimethylbenzothiazolium quaternary salt exists in form of a dimer. The ^{1}H and ^{19}F NMR spectra of methylene base **7** have proved that it also forms a dimer **10**.



Dimer **10** is less stable than nonfluorinated analog but it can be isolated in the Ar atmosphere in form of the light-yellow crystals that decompose at 95–100 °C. GC–MS mass-spectra of dimer **10** corresponds with the monomer, but both monomer and dimer structures were indicated in mass-spectrum verified by LC–MS. It is significant that dimer structures of methylene bases act like monomers [19,30] in reactions with quaternary salts.



Scheme 6.

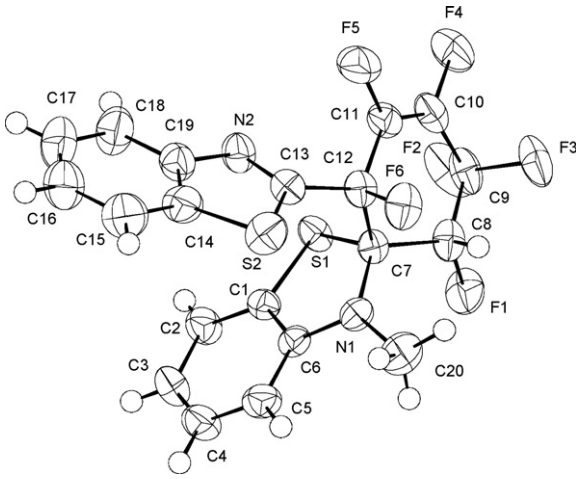


Fig. 1. The perspective view of the molecule **12**. The selected bond lengths (Å) and angles (°): S(1)–C(1) 1.757(3), S(1)–C(7) 1.846(3), S(2)–C(13) 1.736(3), S(2)–C(14) 1.725(4), C(7)–C(8) 1.530(5), C(7)–C(12) 1.570(4), C(8)–C(9) 1.502(5), C(9)–C(10) 1.471(5), C(10)–C(11) 1.302(5), C(11)–C(12) 1.494(5), C(12)–C(13) 1.507(5); S(1)C(7)C(12) 110.2(2), C(7)C(8)C(9) 113.5(3), C(7)C(12)C(11) 110.6(3), C(8)C(9)C(10) 113.0(3), C(9)C(10)C(11) 124.3(4), C(10)C(11)C(12) 123.5(3), C(12)C(13)S(2) 119.6(3).

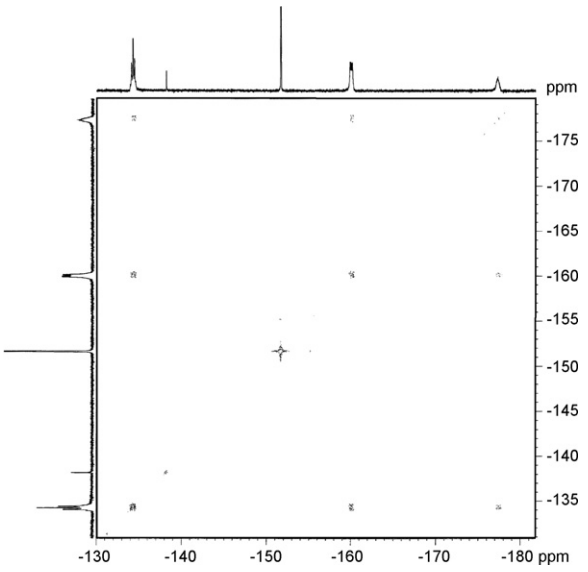


Fig. 2. The ^{19}F–^{19}F COSY spectrum of compound **8**.

Fluoromethylene base **7** has been introduced into reaction with benzothiazole **1** to give an unpredictable result. In the ^{19}F NMR spectra of reaction mixture along with minor signals of expected dye base **11** we detected signals of major product that was isolated and identified by X-ray structure analysis as compound **12**. Formation of it may be explained by the elecrocyclization [35] of the system of double conjugated bonds with 6-π ē of compound **11** into appropriate cyclohexadiene followed by HF addition (Scheme 6).

The perspective view of the molecule **12** and selected geometrical parameters are given in Fig. 1. The C(13)S(2)C(14)C(19)N(2) heterocycle is almost planar – the average deviation from the least-square plane does not exceed 0.003 Å, whereas, the C(1)C(6)N(1)C(7)S(1) heterocycle is less planar (the deviation from the least-square plane achieves 0.101 Å) and has an *envelop* conformation: atoms C(1)C(6)N(1)S(1) are planar within 0.006 Å, and the "corner" S(1)C(7)N(1) forms with this plane the dihedral angle of 15.69°. The N(1) atom has a trigonal-planar bond configuration (sum of the bond angles 359.9°). The C(7)C(8)C(9)C(10)C(11)C(12) cycle is not planar (the deviation from the least-square plane achieves 0.347 Å) and has a *half-boat* conformation: the atoms C(8–12) are coplanar within 0.059 Å, the tetrahedral angle between the planes C(8)C(9)C(10)C(11)C(12) and C(8)C(7)C(12) being 48.7°.

Alkylation of compound **12** by CH_3I in the presence of $AgBF_4$ leads to the formation of quaternary salt **13** that eliminate HF under the action of *p*-diethylaminotoluidine followed by recyclization that led to the desired key dye **8** with λ_{max} = 691 nm – the first representative of the dicarbocyanine dyes with completely fluorinated polymethine chain (Scheme 7).

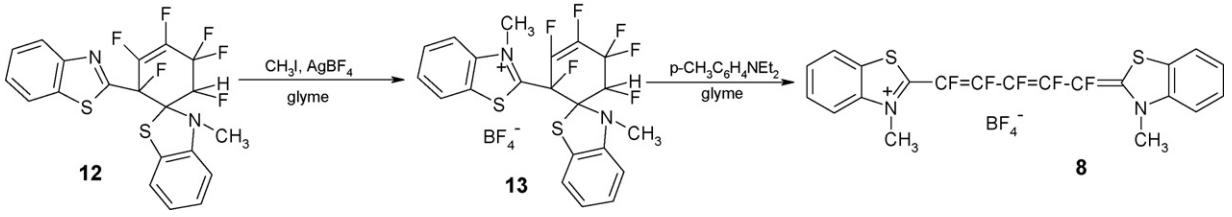
^{19}F NMR spectra data of dye **8** shows that there are three spin-bonded groups of fluorine atoms in molecule **8**. In this spectrum we can see even ^4J coupling constants. There are cross-peaks among all fluorine atoms in ^{19}F–^{19}F COSY spectrum of **8** (Fig. 2). These facts prove the presence of fluorinated polymethine chain in this compound.

Comparison of absorption spectra of dicarbocyanine **8** and the earlier obtained carbocyanine **18** that contains trifluoromethine chain shows a sufficient absorption maximum shift to the long-wave area ($\Delta\lambda_{max}$ = 111 nm) due to the polymethine chain elongation on the CF=CF-fragment (Table 1).

According to calculations it has been assumed that the difluorovinylene shift in dyes with open chain should surpass 100 nm [8]. The assumption was verified for dyes **18** (Δ 125 nm), **21** (Δ 116 nm) and in case of dimethylaminopolyfluoromethine dyes (Δ 121 nm) [7]. Our results have proved the correctness of the calculations.

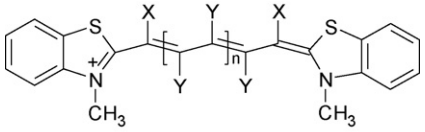
Dye **8** is coloured 41 nm deeper than dicarbocyanine **19** that contains no fluorine atoms. According to the FDK rule the polymethine chain of dye **8** has three colour depressing fluorine atoms at uneven positions (α,γ,ω) and two colour accelerating atoms at β,δ-positions. Comparison of λ_{max} of dyes **18** and **14** shows the bathochrome shift equal to 20 nm. Two α and γ fluorine atoms depress colour, the other one in β-position accelerates the colour. The drastic effect of fluorine atoms at the uneven positions upon dyes colour is explained in publication [12]. It is stated that the conjugation effect of substituents in polymethine chain surpasses five times their inductive effect.

Absorption maxima of dyes **8** and **21**, **19** and **20** show the bathochromic colour shift effect of fluorine atoms at α,ω-positions in pentamethine chain equal to 26–27 nm. In carbocyanine series comparison of λ_{max} of dyes **14** and **16** shows value of 23 nm. Thus,



Scheme 7.

Table 1
Absorption maxima of cyanine dyes with fluorine atoms and fluoroalkyl groups in chain.



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No.	*n*	*X*	*Y*	λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)[a]	Reference
14	0	H	H	558		[2]
15	0	H	F	522		[37]
16	0	F	H	605	47:2 = 23.5 (14)	[17]
17	0	H	CF_3	581		[37]
18	0	F	F	578	125[b]	[16]
9	0	F	$CHFCF_3$	660	79 (17) 82 (18)	[38]
19	1	H	H	650		[36]
20	1	F	H	703	53:2 = 26.5 (19)	[17]
21	1	H	F	637	116 (15)	[20]
8	1	F	F	691	111 (18) 54:2 = 27 (21) 41 (19)	

An−: anion minus.
[a] Number of dye chosen for comparison is given in parenthesis.
[b] Comparison with iodide bis-[3-etylbenzothiazol-2-yl]-8-fluoromethinecyanine λ_{max} = 453 nm [2].

in compliance with the FDK rule fluorine atoms at α,γ- and α,ω-positions depress dyes colour, and depression values are very close.

Due to the FDK rule dye **9** with $CHFCF_3$ electron-withdrawing group in β-position has a more deep colour than dye **18** with completely fluorinated polymethine chain. Previously Yagupolskii and co-workers on discussing spectrochemical properties of carbocyanines with fluorine atom in α-position and fluoroalkyl groups in β-position has shown that such dyes demonstrate effect of substituents interaction. Their shift of absorption bands to long waves area sufficiently surpasses the shifts sum of corresponding mono-substituted dyes [3,38]. The colour of the dye **9** also proves this fact.

3. Conclusion

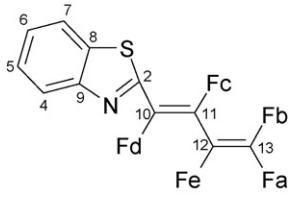
In summary, here we report the way to prepare the first representative of dicarbocyanine dyes with completely fluorinated polymethine chain. The main precursor to reach the goal – 2-perfluorobutadienyl benzotiazole **1** – was obtained via the Stille coupling of 2-iodobenzotiazole with perfluorobutadiene that opens the way to 2-perfluorobutadienyl heterocycles series. Electrocyclization of compound **1** with fluoromethylene benzotiazole base led to cyclic product that transforms into open chain cyanine dye **8** after quaternization and base action.

The results of fluorescence properties investigations of various cyanine dyes with perfluorinated polymethine chain as well as structure and aggregation peculiarities will be reported in due coarse.

4. Experimental

All reactions were carried out under anhydrous argon atmosphere in annealed glassware using freshly distilled solvents such as pentane, hexane (distilled over P_2O_5), THF (freshly distilled over Na/benzophenone), ether (double-distilled over $LiAlH_4$ and kept over CaH_2), acetonitrile (distilled over P_2O_5 and CaH_2), nitromethane, dichloroethane (distilled over P_2O_5 and freshly annealed K_2CO_3), and chloroform (washed with a solution of K_2CO_3, dried over $MgSO_4$, and distilled over freshly annealed K_2CO_3). A 2.5N solution of BuLi in hexane and Bu_3SnCl were provided by Aldrich and Acros, respectively. Single crystals of **12** were obtained from pentane, mounted in inert oil, and transferred to the cold gas stream of the diffractometer. Whenever possible the reactions were monitored by thin-layer chromatography (TLC). TLCs were run on Merck Kieselgel 60 F_{254} plates. Purification of some products was carried out using column chromatography (CC) on Silica gel, 70–230 mesh 60A (Aldrich) or Al_2O_3 90 neutral acc. II-III by Brockmann, *M* = 101 g/mol (Merck). Electronic absorption spectra were recorded on a spectrophotometer Specord M40. ^{13}C NMR spectra were recorded on a Bruker DRX 500 instrument at 125 MHz, ^1H and ^{19}F NMR spectra were recorded at 299.9 and 188.1 MHz, respectively, with a Varian VXR-300 spectrophotometer, and chemical shifts are given in ppm relative to Me_4Si and CCl_3F, respectively, as internal standards. 1D ^{19}F spectra and 2D ^{19}F–^{19}F COSY were obtained at room temperature in CD_3CN solution on a Varian Unity 400 Spectrometer. LC–MS spectra were registered on "Agilent 1100 Series" instrument with diode-matrix and mass-selective detector "Agilent 1100 LS/MSD SL" (ionization method–chemical ionization at atmospheric pressure; ionization chamber operation conditions – simultaneous scanning of positive and negative ions in the range 80–1000 *m/z*). Melting points are uncorrected and were measured with electro thermal apparatus. Elemental analysis was performed in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kiev.

4.1. 2-Pentafluorbuta-1,3-dienyl-benzothiazole (1)



A reactor, equipped with, a magnetic stirrer, rubber septum and thermometer was charged with a solution of $Pd(PPh_3)_4$ (0.86 g, 0.75 mmol) and 2-iodobenzothiazole (1.96 g, 7.5 mmol) [39] in THF (40 ml). The solution was slowly heated to 40 °C and maintained for 5 min at this temperature. The reaction mixture was then cooled to 0 °C. Copper (I) iodide (1.43 g, 7.5 mmol) was added all at once and the solution of stannane **4** (4.87 g, 11.25 mmol) in THF (20 ml) was slowly added over 40 min via syringe. The reaction mixture was maintained at 0 °C for 30 min, then was heated to r.t. for 30–40 min and stirred at 38–40 °C for 20 h. THF was evaporated in vacuum and the residue was extracted with hexane (3× 15 ml). The precipitate formed was filtered and washed with hexane (15 ml). The hexane solution was concentrated to 15 ml and chromatographed on silica gel. The impurities were eluated with hexane and the product **1** – with the mixture hexane:benzene (10:3). Yield: 1.39 g (66.8%); m.p. 77–78 °C. ^1H NMR (299.9 MHz, $CDCl_3$): δ 7.49–8.20 (4H, m, Ar); ^{19}F NMR (188.1 MHz, $CDCl_3$): δ −90.7 (dd, 1F, ^2J = 48.7 Hz, ^3J = 31.5 Hz, F^a), −103.1 (dddd, 1F, ^2J = 48.7 Hz, ^3J = 115.4 Hz, ^4J = 24.3 Hz, ^5J = 13.7 Hz, F^b), −145.1 (ddt, 1F, ^3J = 130.4 Hz, ^4J = 24.3 Hz, ^3J = 12.5 Hz, F^c), −150.3 (ddd, 1F, ^3J = 130.4 Hz, ^4J = 31.5 Hz, ^5J = 13.7 Hz, F^d), −184.0 (dtd, 1F, ^3J = 115.4 Hz, ^3J = 31.5 Hz, ^3J = 12.5 Hz, F^e); ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.8 (dd, ^2J = 25 Hz, ^3J = 11.5 Hz, C_2), 153.8 (dddm, ^1J = 343 Hz, ^1J = 291 Hz, ^2J = 50.0 Hz, C_{13}), 152.5 (s, C_9), 145.5 (ddm, ^1J = 247 Hz, ^2J = 43.8 Hz, C_{10}), 140.5 (dddm, ^1J = 250 Hz, ^2J = 47 Hz, ^2J = 25 Hz, C_{11}), 135.0 (s, C_8), 127.2 (s, C_5), 126.8 (s, C_6), 124.5 (s, C_7), 121.5 (s, C_4), 119.5 (ddm, ^1J = 231 Hz, ^2J = 49.6 Hz, C_{12}). Anal. Calcd. for $C_{11}H_4F_5NS$: C 47.6, H 1.4. Found C 47.7, H 1.4. MS (*m/z*): 277 $[M]^+$.

4.2. Tributyltrifluorovinylstannane (2)

A reactor, equipped with magnetic stirrer, rubber septum, thermometer and dropping funnel was charged with ether (100 ml) and THF (100 ml). Freon 134a (CF_3CH_2F) (27.5 g, 0.27 mol) was condensed at temperature conditions from −35 °C to −85 °C. Then the solution of LiN^iPr_2 obtained from the reaction between the 2.5N solution of BuLi in hexane (112 ml, 0.28 mol) in THF (130 ml), and HN^iPr_2 (28 g, 0.28 mol) [40] was added dropwise at −78 to −80 °C for 20 min. The reaction mixture was additionally stirred for 1 h at this temperature and then Bu_3SnCl (41 g, 0.125 mol) was slowly added over 20 min via syringe. The reaction mixture was washed with ice water (500 ml) and extracted with ether (3× 150 ml). The ether extracts were combined, washed with water (3× 50 ml) and dried over magnesium sulfate. Ether was evaporated. The crude stanane **2** (45 g) was chromatographed with pentane (300 ml) on silica gel. Pentane was evaporated, residue was purified by distillation in vacuum. Yield: 40 g (85.6%); b.p. 91–92 °C (0.5 mm Hg), n_D^{20} 1.4530, in the literature n_D^{25} 1.4512 [27]. ^1H, ^{19}F and ^{13}C NMR spectra are consistent with literature data [23].

4.3. Trans-triethyl(pentafluoro-1,3-butadienyl)silane (3)

The solution of *trans*-(1,2-difluoro-2-iodvinyl)trietylsilane [24] (21.3 g, 70 mmol) and $Pd(PPh_3)_4$ (4.04 g, 3.5 mmol) in DMF (220 ml) was slowly heated to 40 °C and maintained for 5 min at this temperature. The reaction mixture was then cooled to 0 °C. Copper (I) iodide (6.7 g, 35 mmol) was added all at once and stannane **2** (32.5 g, 87.5 mmol) was slowly added over 2 h via syringe. The reaction mixture was maintained at 0 °C for 30 min then was heated to r.t. for 30–40 min and stirring for 20–25 h (monitored by ^{19}F NMR spectra). Reaction mixture was added to saturated brine solution (700 ml) and extracted with ether (3× 200 ml). The ether extracts were combined, washed with water and dried over magnesium sulfate. Ether was evaporated and the residue was purified by fractional distillation. Yield: 14.6 g (80.7%); b.p. 63–65 °C (15 mm Hg), n_D^{18} 1.4145. ^1H, ^{19}F and ^{13}C NMR spectra are consistent with literature data [23].

4.4. 2-(Pentafluoro-1,3-butadienyl)-3-methyl benzothiazolium tetrafluoroborate (5)

The solution of benzothiazole **1** (0.9 g, 3.25 mmol) and CH_3I (1.38 g, 9.75 mmol) in dichlorethane (20 ml) was cooled with ice and $AgBF_4$ (0.92 g, 4.72 mmol) was added all at once. The reaction mixture was additionally stirred at r.t. for 12 h. The solvent was evaporated in vacuum without heating and the residue was dried in vacuum at 30 °C for 4 h. Then nitromethane (12 ml) was added in dry box and the precipitate formed (AgI) was filtered off. The reaction solution was concentrated to 2–2.5 ml and salt **5** was precipitated with dry ether (30 ml). The solvent was decanted and the residue was dried in vacuum. Yield: 1.01 g (82.1%); m.p. 107–110 °C (dec.). ^{19}F NMR (188.1 MHz, CH_3NO_2): δ −85.1 (m, 1F), −97.4 (dm, 1F, J = 110.7 Hz), −138.4 (dm, 1F, J = 132.4 Hz), −144.5 (dm, 1F, J = 132.4 Hz), −151.7 (s, 4F, BF_4), −188.7 (dm, 1F, J = 110.7 Hz). Salt **5** was applied to synthesis of dyes without the further purification.

4.5. 2-Fluoromethyl-3-methyl-benzothiazol-3-ium tetrafluoroborate (6)

The stirred mixture of 2-fluoromethylbenzothiazole (5.86 g, 35.2 mmol) [41] and dimethylsulfate (45 g, 35.7 mmol) was heated at 90–100 °C for 7 h. The reaction mixture was washed with benzene and dried. The residue was dissolved in water (20 ml) and mixed with water solution (10 ml) of $NaBF_4$ (10.3 g, 93.6 mmol). The precipitate formed (salt **6**) was filtered off, dried and crystallized from ethanol. Yield: 8.5 g (90%); m.p. 167–169 °C. ^1H NMR (299.9 MHz, [D_6]DMSO): δ 7.86–8.54 (4H, m, Ar), 6.37 (2H, d, J = 44.3 Hz), 4.22 (3H, s, CH_3); ^{19}F NMR (188.1 MHz, [D_6]DMSO): δ −148.5 (s, 4F, BF_4), −221.2 (t, 1F, J = 44.3 Hz).

4.6. 2-Fluoromethylene-3-methyl-2,3-dihydro-benzothiazole (7) dimer (10)

To the suspension of salt **6** (0.67 g, 2.5 mmol) in DME (15 ml) NaH (0.2 g, 5 mmol, 60% in mineral oil) was added. The reaction mixture was stirred at r.t. for 20 h and filtered off in argon atmosphere. The formation of product **7** was monitored by ^{19}F NMR spectra (relatively to PhF) to reach 95% yield. DME was evaporated in vacuum and the residue was extracted with hexane (40 ml). The extract was concentrated to 10 ml and cooled. The precipitate formed was filtered off and dried in vacuum. Yield: 0.32 g (71%); m.p. 109–115 °C (dec.). ^1H NMR (299.9 MHz, $CDCl_3$): δ 6.44–7.12 (8H, m, Ar ×2), 4.69 (2H, dm, ^2J = 47.9 Hz, CH_2F), 3.54 (3H, s, CH_3), 2.92 (3H, s, CH_3); ^{19}F NMR (188.1 MHz, $CDCl_3$): δ −156.8 (s, 1F), −208.5 (t, 1F, ^2J = 47.9 Hz). Anal. calcd. for $C_{18}H_{16}F_2N_2S_2$: C 59.6, H 4.4. Found C 59.6, H 4.5. GC–MS (m/z): 181 $[M]^+$ (monomer); LC–MS (m/z): 181 $[M]^+$ (monomer) and 362 $[M]^+$ (dimer).

4.7. 3-Methyl-1′,2′,3′,3′,4′,6′-hexafluoro-6′-(benzotiazole-2-yl)-3H-spiro[benzotiazole-2,5′-cyclohexene] (12)

To the solution of benzothiazole **1** (0.2 g, 0.72 mmol) in DME (3 ml) the solution of base **7** (2.16 mmol) in DME was slowly added over 15 min via syringe at −10 °C. The solution was slowly (over 1 h) heated to r.t. and additionally stirred for 10 h. DME was evaporated in vacuum and the residue was extracted with hexane (3× 25 ml). The extract was concentrated to 20 ml and chromatographed on Al_2O_3. The impurities were eluated with hexane (50 ml) and the product **12** – with benzene (70 ml). The solvent was evaporated in vacuum. Yield: 0.24 g (72.7%); m.p. 118–119 °C (from hexane). ^1H NMR (299.9 MHz, $CDCl_3$): δ 7.32–8.05 (4H, m, Ar), 6.16–6.72 (4H, m, Ar), 5.76 (1H, dt, ^2J = 47.8 Hz, ^3J = 10.3 Hz); ^{19}F NMR (188.1 MHz, $CDCl_3$): δ −110.3 (m, 2F), −135.1 (m, 2F), −154.2 (m, 1F), −212.0 (dt, 1F, ^2J = 47.8 Hz, ^3J = 16.7 Hz). MS (m/z): 458 $[M]^+$.

X-ray structure determination of **12**.

Crystal data: $C_{20}H_{12}F_6N_2S_2$, M = 458.44, orthorhombic, space group *Pbca*, a = 16.1698(10), b = 9.0647(6), c = 30.231(2) Å, V = 4431.0(5) Å^3, Z = 8, d_c = 1.374 g cm^{-3}, μ = 0.298 mm^{-1}, F(0 0 0) = 1856, crystal size ca. 0.15 mm × 0.18 mm × 0.41 mm. All crystallographic measurements were performed at 173(1) K on a Bruker Smart Apex II diffractometer operating in the ω and φ scans mode. The intensity data were collected within the range of $1.8^\circ \le \theta \le 26.4^\circ$ using Mo-K_α radiation (λ = 0.71078 Å). The intensities of 13174 reflections were collected (4480 unique reflections, R_{int} = 0.031). The SADABS absorption correction (the ratio of minimum to maximum apparent transmission is 0.59) was applied. The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for the non-hydrogen atoms using the SHELXS97 and SHELXL97 programs [42,43]. During the structure refinement, the atoms of the disordered solvent molecule were observed by inversion center, but could not be modeled satisfactorily. The SQUEEZE routine in PLATON (potential solvent accessible area volume 693 Å^3) was used to modify the HKL file and the solvent equated to half molecule of glime per molecule of compound.

Hydrogen atoms were placed at the calculated positions. In the refinement 4480 independent reflections (2866 reflections with $I \geq 2\sigma(I)$) were used. Convergence was obtained at $R_1 = 0.1058$ and $wR_2 = 0.1614$ for all reflections, and $R_1 = 0.0637$ and $wR_2 = 0.1417$ for observed, GOF = 1.057 (272 parameters; observed/variable ratio 10.5); the largest and minimal peaks in the final difference map 0.36 e/Å^3 and −0.19 e/Å^3, weighting scheme is as follows: $\omega = 1/[\sigma^2(Fo^2) + (0.0746P)^2 + 1.3690P]$, where $P = (Fo^2 + 2Fc^2)/3$. Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (741117).[1] Any request to the 741117 for these materials should quote the full literature citation and reference number 741117.

4.8. Tetrafluoroborates of 3-methyl-1′,2′,3′,3′,4′,6′-hexafluoro-6-(benzotiazole-2-yl)-3H-spiro [3-methylbenzotiazole-2,5′-cyclohexene] (**13**)

To the solution of cycle **12** (0.32 g, 0.7 mmol) and CH_3I (0.3 g, 2.1 mmol) in DME (5 ml) $AgBF_4$ (0.2 g, 1.03 mmol) was added in dry box and the reaction mixture was stirred for 5 h. The precipitate formed was filtered off in dry box and washed with DME (5 ml). Crude residue was washed with dry nitromethane (2× 3 ml). The received solution was concentrated in vacuum without heating to 1.5–2 ml and salt **13** was precipitated with ether (40 ml) and dried in vacuum for 2 h. Salt **13** (0.18 g, 49% yield) was used in synthesis of dye **8** without purification.

4.9. 3-Methyl-2-[1,2,3,4,5-pentafluoro-5-(3-methyl-3H-benzothiazol-2-ylidene)-penta-1,3-dienyl]-benzothiazol-3-ium tetrafluoroborate (**8**) and 3-methyl-2-{1,3,4,4,4-pentafluoro-2-[fluoro-(3-methyl-3H-benzothiazol-2-ylidene)-methyl]-but-1-enyl}-benzothiazol-3-ium tetrafluoroborate (**9**)

(a) The suspension of salt **5** (0.126 g, 0.33 mmol) in DME (1 ml) was cooled to 0 °C and obtained in situ solution of base **7** (0.12 g, 0.66 mmol) was added via syringe. The reaction mixture was additionally stirred for 30 min at 0 °C and then for 2 h at r.t. The mixture of dyes was precipitated with dry ether (30 ml). The precipitate formed was filtered off and chromatographed on silica gel. The impurities were eluated with dry $CHCl_3$ and dyes **8** and **9** – by the mixture of $CHCl_3$:CH_3CN (10:3). The solvent was evaporated in vacuum. Dye **9** was extracted with DME and the precipitate of dye **8** was washed with $CHCl_3$ and dried in vacuum. Yield (**8**) 0.03 g (16.7%), m.p. 160–165 °C (dec.), λ_{max}(CH_3CN)/nm 691, ε 4.2 × 10^4 l/(mol cm) в CH_3CN. ^{1}H NMR (299.9 MHz, [D_6]DMSO): δ 7.53–8.17 (8H, m, 2× Ar), 4.04 (6H, s, 2× CH_3); ^{19}F NMR (376.3 MHz, CD_3CN): δ −134.2 (t, 2F, ^3J = 70 Hz, 2× βF), −160.0 (dd, 2F, ^3J = 70.0 Hz, ^4J = 35 Hz, 2× αF), −151.7 (s, 4F, BF_4), −177.3 (m, 1F, γF). Anal. calcd. for $C_{21}H_{14}BF_9N_2S_2$: C 46.6, H 2.6. Found C 46.8, H 2.7; yield: (**9**) 0.04 g (21.5%), m.p. 132–133 °C (dec.), λ_{max}(CH_3CN)/nm 660, ε 2.5 × 10^4 l/(mol cm) в CH_3CN. ^{1}H NMR (299.9 MHz, $CDCl_3$): δ 7.31–7.69 (8H, m, 2× Ar), 6.0 (1H, dq, ^2J = 43.9 Hz, ^3J = 12.6 Hz, –C**H**FCF$_3$), 3.9 (6H, s, 2× CH_3); ^{19}F NMR (188.1 MHz, $CDCl_3$): δ −75.1 (dd, 3F, ^2J = 28.1 Hz, ^2J = 12.6 Hz, –CHFC**F$_3$**), −129.6 (m, 2F, 2× =CF), −151.6 (s, 4F, BF_4), −203.2 (dq, 1F, ^2J = 43.9 Hz, ^3J = 12.6 Hz, –CH**F**CF$_3$). Anal. calcd. for $C_{21}H_{15}BF_{10}N_2S_2$: C 45.0, H 2.6. Found C 45.2, H 2.7.

(b) To the suspension of salt **13** (0.11 g, 0.2 mmol) in DME (2 ml) the solution of *p*-diethylaminotoluidine (0.32 g, 0.2 mmol) in DME (2 ml) was added. In 3 min CH_3CN (1 ml) was added and the reaction solution was stirred for 30 min. Dye was precipitated with dry ether (30 ml), filtered off and chromatographed with the mixture of $CHCl_3$:CH_3CN (10:4) on silica gel. Yield: (**8**) 0.03 g (30%). λ_{max}(CH_3CN)/nm 691. ^{1}H, ^{19}F and ^{13}C NMR spectra are consistent with dye **8**.

[1] CCDC-741117 contains the supplementary crystallographic data for compound 12. These data can be obtained free of charge via www.ccdc.cam.uk/const/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK); fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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