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NOVEL FLUORINE CONTAINING TETRATHIAFULVALENES FOR THE PREPARATION OF LANGMUIR–BLODGETT FILMS

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The novel fluorinated tetrathiafulvalenes: tetra(2,3,5,6-tetrafluorobenzylthio)-, dimethyldi(2,3,4,5,6-pentafluorobenzylthio)-, dimethyldi(2,3,5,6-tetrafluorobenzylthio)-, dimethyldi[3,5-di(trifluoromethyl)-benzylthio]-, and dimethyldi(2-fluoro-4-bromobenzylthio)tetrathiafulvalenes have been synthesized in order to prepare Langmuir–Blodgett films. Their cyclic voltamograms have been studied and these show two, reversible, one-electron oxidation waves. A novel series of fluorinated benzylthio- and benzoylthio-1,3-dithiole-2-thiones and -2-ones has been synthesized.

Keywords: 1,3-dithiol-2-ones, 1,3-dithiole-2-thiones, fluorinated benzylthiotetrathiafulvalenes, cyclic voltamograms.

In recent times an increasing amount of attention has been focused on studying the electroconductive properties of organic conductors derived from mono- and multifilms prepared by the Langmuir–Blodgett method (LB films). These conducting LB films were previously obtained based on amphiphilic 7,7,8,8-tetracyanoquinodimethane (TCNQ) and tetrathiafulvalene (TTF) derivatives which contained long aliphatic chains [1-3]. However, in recent times, it has been possible to prepare films based on TTF derivatives not containing long chains [4] with their stabilization brought about by the addition of aliphatic acids such, for example, as arachidonic acid [2-4]. In the studies [2, 3] tetra(benzylthio)tetrathiafulvalene was used for the preparation of the conducting films and di(methylthio)di(benzylthio)tetrathiafulvalene in the report [5]. The exchange of hydrogen for fluorine in the benzyl radical and the effect of this exchange on the stability of the LB film had not been investigated at all hence we have prepared a novel series of fluoro-substituted benzylthiotetrathiafulvalenes. The synthesis of the latter has been performed according to Scheme 1 starting from the mesoionic salt **1** which was prepared by the methods reported in the studies [6-9]. Alkylation of the salt **1** was carried out with the fluoro-substituted benzyl chlorides or bromides in acetone by heating to the disappearance of its orange coloration. As a rule, the obtained chlorides (**2a,c** – oil, and **2b,d** – crystals) can be used for further syntheses without purification. Reduction of these compounds occurs most efficiently in acetonitrile medium using a small excess of sodium borohydride. The 2-substituted 1,3-dithioles **3a-d** obtained in this way are oily products which can also be used without preliminary purification. The 1,3-dithiolium perchlorates **4a-d** are crystalline products which decompose upon heating.

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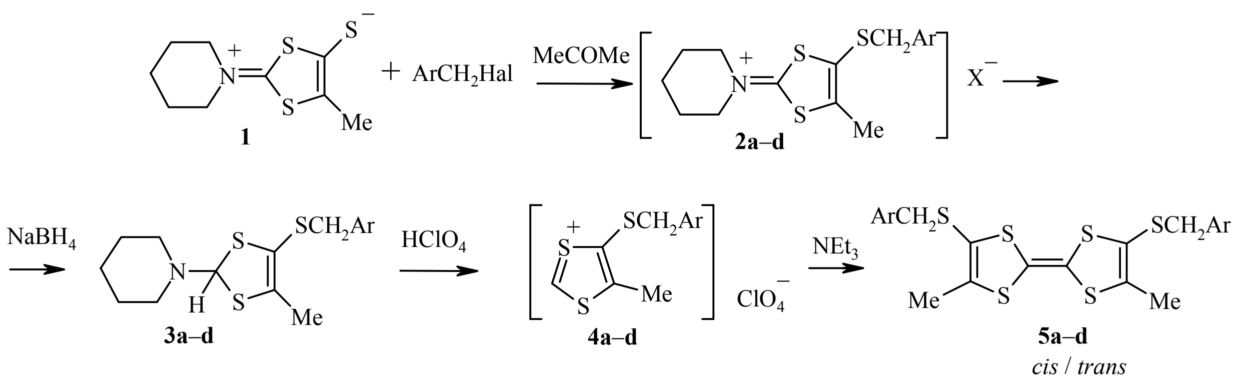
Scheme 1

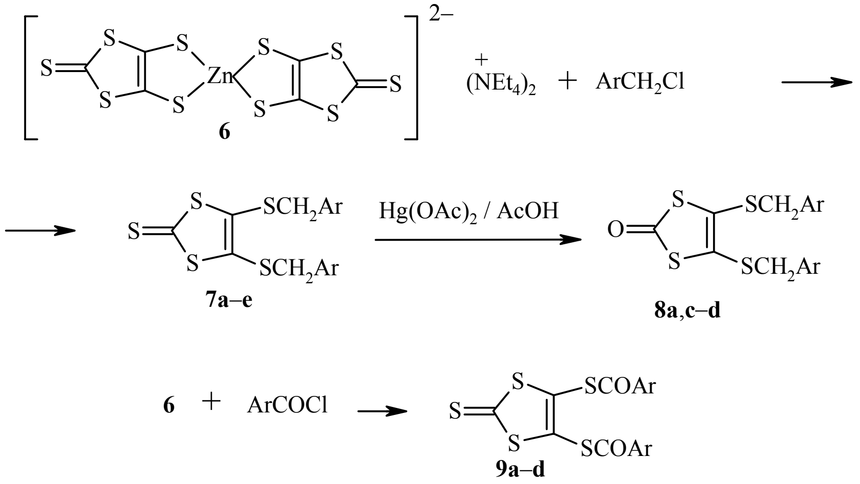


2–**5 a** Ar = C_6F_5, **b** Ar = 2,3,5,6-F_4C_6H, **c** Ar = 3,5-$(CF_3)_2C_6H_3$, **d** Ar = 2-F,4-Br–C_6H_3;
2 a, **b**, **d** X = Cl, **c** X = Br

The tetrathiafulvalenes **5a-d** synthesized were obtained as a mixture of the *cis* and *trans* forms and are orange colored crystalline materials.

Alkylation of the bistetraethylammonium bis(1,3-dithiole-2-thione-4,5-dithiolato) zincate (**6**), which had been obtained by the method reported in [10], with the fluoro-substituted benzyl chlorides in acetone gave the 4,5-di(2,3,5,6-tetrafluorobenzylthio)- (**7a**), 4,5-di(2,3,4,5-tetrafluorobenzylthio)- (**7b**), 4,5-di(2,3,4,5,6-pentafluorobenzylthio)- (**7c**), 4,5-di(2-fluoro-4-bromobenzylthio)- (**7d**), and 4,5-di[3,5-di(trifluoromethyl)-benzylthio]-1,3-dithiole-2-thione (**7e**) (see Scheme 2). Upon heating with mercuric acetate for 5-10 min in acetic acid they are converted to 4,5-di(2,3,5,6-tetrafluorobenzylthio)- (**8a**), 4,5-di(2,3,4,5,6-pentafluorobenzylthio)- (**8c**), 4,5-di(2-fluoro-4-bromobenzylthio)- (**8d**), and 4,5-di[3,5-di(trifluoromethyl)benzylthio]-1,3-dithiol-2-one (**8e**) respectively. The obtained oxygen derivatives do not form the corresponding tetrathiafulvalenes when heated in triethylphosphite.

Scheme 2

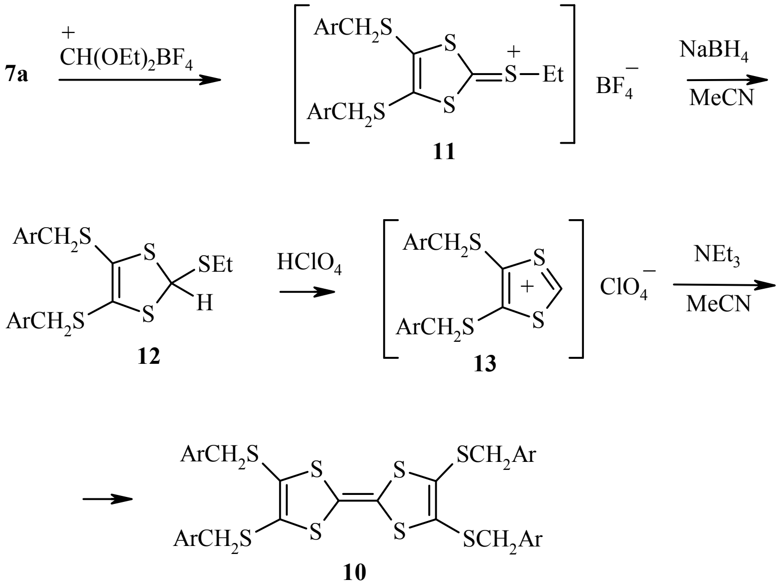


7, **8 a** Ar = 2,3,5,6-F_4C_6H; **b** Ar = 2,3,4,5-F_4C_6H; **c** Ar = C_6F_5; **d** Ar = 2-F,4-Br–C_6H_3;
e Ar = 3,5-$(CF_3)_2C_6H_3$; **9 a** Ar = 3-F–C_6H_4; **b** Ar = 2,3,4-$F_3C_6H_2$; **c** Ar = 2,3,4,5-F_4C_6H;
d Ar = 3,5-$(CF_3)_2C_6H_3$

The reaction of the zincate **6** with the fluoro-substituted benzoyl chlorides (see Scheme 2) also gave 4,5-di(3-fluorobenzoylthio)- (**9a**), 4,5-di(2,3,4-trifluorobenzoylthio)- (**9b**), 4,5-di(2,3,4,5-tetrafluorobenzoylthio)- (**9c**), and 4,5-di[3,5-di(trifluoromethyl)benzoylthio]-1,3-dithiole-2-thione (**9d**) which could not be converted to the corresponding tetrathiafulvalenes by the standard methods.

Following Scheme 3 [11], the thione **7a** gave the tetra(2,3,5,6-tetrafluorobenzylthio)tetrathiafulvalene (**10**). Reaction of compound **7a** with diethoxycarbenium borofluoride in methylene chloride gave the 2-ethylthio-4,5-di(2,3,5,6-tetrafluorobenzylthio)-1,3-dithiolium borofluoride (**11**). The latter was reduced using sodium borohydride in acetonitrile to give 2-ethylthio-4,5-di(2,3,5,6-tetrafluorobenzylthio)-1,3-dithiole (**12**) which could be treated with perchloric acid in ether to give the 4,5-di(2,3,5,6-tetrafluorobenzylthio)-1,3-dithiolium perchlorate (**13**). The reaction of perchlorate **13** with triethylamine in acetonitrile gave the tetrathiafulvalene (**10**) as small, dark red needles.

Scheme 3



10–13 Ar = 2,3,5,6-F_4C_6H

The characteristics for the synthesized compounds are given in Table 1.

Since compounds **2a,c, 3a,c,d, 4a-d, 12,** and **13** were used in subsequent syntheses without purification their parameters are not reported in Table 1.

In order to measure the electron-donor properties of the synthesized fluoro-containing tetrathiafulvalenes we obtained their cyclic voltamperograms and observed two reversible, one-electron oxidation waves. Their potentials are given in Table 2. Comparison with the unsubstituted tetrathiafulvalene shows that the oxidation of the fluoro-substituted benzylthiotetrathiafulvalenes occurs at higher potentials. The even higher value of $E_{1/2}^1$ for compound **10** can be explained by the presence of the four bulky tetrafluorobenzyl substituents around the central tetrathiafulvalene fragment which hinders the process of oxidation of the latter.

The obtained compounds could be used for the synthesis of the conductive cation radical salts and for the formation of LB films.

TABLE 1. Characteristics of the Synthesized Compounds

Com-pound	Empirical formula	$\frac{\text{Found S, \%}}{\text{Calculated S, \%}}$	mp, °C	IR spectrum, ν, cm^{-1}	^{1}H NMR (CDCl$_3$), δ, ppm
1	2	3	4	5	6
2b	$C_{16}H_{16}ClF_4NS_3$	$\frac{22.30}{22.37}$	111-112		1.65 (6H, m, 3CH$_2$); 1.67 (3H, d, CH$_3$); 3.50 (2H, s, SCH$_2$); 4.53 (4H, m, 2NCH$_2$); 7.03 (1H, m, H$_{Ar}$)
2d	$C_{16}H_{18}BrFNS_3$	$\frac{21.07}{21.14}$	162-163		1.84 (2H, s, CH$_2$); 1.96 (4H, m, 2CH$_2$); 2.02 (3H, s, CH$_3$); 4.00 (6H, m, 2NCH$_2$, SCH$_2$); 7.30 (3H, m, H$_{Ar}$)
3b	$C_{16}H_{17}F_4NS_3$	$\frac{24.25}{24.32}$	88-89		1.45 (2H, m, CH$_2$); 1.57 (4H, m, 2CH$_2$); 2.52 (4H, m, 2CH$_2$); 2.02 (3H, s, CH$_3$); 3.97 (2H, s, SCH$_2$); 5.95 (1H, s, CH); 6.99 (1H, m, H$_{Ar}$)
5a	$C_{22}H_{10}F_{10}S_6$	$\frac{29.15}{29.29}$	165-167		2.00 (6H, s, 2CH$_3$); 3.95 (4H, s, 2CH$_2$)
5b	$C_{22}H_{12}F_8S_6$	$\frac{30.85}{30.99}$	181-182		2.00 (6H, s, 2CH$_3$); 3.99 (4H, s, 2CH$_2$); 7.01 (2H, m, H$_{Ar}$)
5c	$C_{26}H_{16}F_{12}S_6$	$\frac{25.53}{25.69}$	135-136		1.73 (6H, s, 2CH$_3$); 3.95 (4H, s, 2CH$_2$); 7.79 (2H, s, H$_{Ar}$); 7.70 (4H, s, H$_{Ar}$)
5d	$C_{20}H_{12}Br_2F_2S_6$	$\frac{28.55}{28.69}$	157-159		1.75 (6H, m, 2CH$_3$); 3.85 (4H, s, 2SCH$_2$); 7.07 (2H, s, H$_{Ar}$); 7.23 (4H, m, H$_{Ar}$)
7a	$C_{17}H_6F_8S_5$	$\frac{30.58}{30.68}$	101-102	1065 (C=S)	4.07 (4H, s, 2CH$_2$); 7.05 (2H, m, H$_{Ar}$)
7b	$C_{17}H_6F_8S_5$	$\frac{30.51}{30.68}$	61-63	1063 (C=S)	4.01 (4H, s, 2CH$_2$); 7.00 (2H, m, H$_{Ar}$)
7c	$C_{17}H_4F_{10}S_5$	$\frac{28.62}{28.70}$	78.5-79.5	1063 (C=S)	4.06 (4H, s, 2CH$_2$)

TABLE 1 (continued)

1	2	3	4	5	6
7d	$C_{17}H_{10}Br_2F_2S_5$	$\frac{27.83}{28.01}$	102-103	1069 (C=S)	3.93 (4H, s, 2CH_2); 7.95 (4H, m, H_{Ar}); 7.09 (2H, m, H_{Ar})
7e	$C_{21}H_{10}F_{12}S_5$	$\frac{24.53}{24.64}$	172-173	1060 (C=S)	4.38 (4H, s, 2CH_2); 7.99 (4H, s, H_{Ar}); 7.97 (2H, s, H_{Ar})
8a	$C_{17}H_6F_8OS_4$	$\frac{25.28}{25.32}$	86-87	1660 (C=O)	4.05 (4H, s, 2CH_2); 7.05 (2H, m, H_{Ar});
8c	$C_{17}H_4F_{10}OS_4$	$\frac{23.53}{23.64}$	46-50	1663 (C=O)	4.03 (4H, s, 2CH_2)
8d	$C_{17}H_{10}Br_2F_2OS_4$	$\frac{22.97}{23.05}$	Oil	1665 (C=O)	3.90 (4H, s, 2CH_2); 7.91 (4H, m, H_{Ar}); 7.0 (2H, m, H_{Ar})
8e	$C_{21}H_{10}F_{12}OS_4$	$\frac{20.10}{20.21}$	79-80	1670 (C=O)	4.35 (4H, s, 2CH_2); 8.37 (4H, s, H_{Ar}); 8.16 (2H, s, H_{Ar})
9a	$C_{17}H_8F_2O_2S_5$	$\frac{36.10}{36.22}$	131-132	1682 (C=O) 1085 (C=S)	7.50 (8H, m, H_{Ar})
9b	$C_{17}H_4F_6O_2S_5$	$\frac{31.09}{31.16}$	123-124	1685 (C=O) 1065 (C=S)	7.69 (2H, m, H_{Ar}); 7.16 (2H, m, H_{Ar})
9c	$C_{17}H_2F_8O_2S_5$	$\frac{29.01}{29.12}$	115-117	1675 (C=O) 1060 (C=S)	7.08 (2H, m, H_{Ar})
9d	$C_{21}H_6F_{12}O_2S_5$	$\frac{23.50}{23.62}$	153-155	1670 (C=O) 1065 (C=S)	8.16 (2H, s, H_{Ar}); 8.37 (4H, s, H_{Ar})
10	$C_{34}H_{12}F_{16}S_8$	$\frac{26.02}{26.15}$	159-161		2.05 (8H, s, 4CH_2); 7.49 (4H, m, H_{Ar})

TABLE 2. Cyclic Voltamperogrametric Data*

Compound	$E_{1/2}^1$, V	$E_{1/2}^2$, V	Compound	$E_{1/2}^1$, V	$E_{1/2}^2$, V
5a	0.55	0.89	Tetrathiafulvalene	0.41	0.82 [12]
5b	0.53	0.89	Tetra(benzylthio)-tetrathiafulvalene	0.57	0.85 [3]
5c	0.51	0.84			
5d	0.48	0.82	Trimethyl(benzylthio)-tetrathiafulvalene	0.27	0.81 [8]
10	0.69	0.94			

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* Voltamperograms were obtained in benzonitrile solution; tetraethylammonium perchlorate (*c* = 0.1 molar) electrolyte, Pt working electrode, AgCl/Cl reference electrode, 50 mV/s scanning rate, 0.1 molar concentration of tetrathiafulvalene.

EXPERIMENTAL

The fluoro-substituted benzyl and benzoyl chlorides were obtained from OOO "Okta" (Perm city). ^{1}H NMR spectra were taken on a DRX-400 spectrometer (400 MHz). IR spectra were recorded on a UR-20 spectrometer using vaseline oil and the cyclic voltamperograms were obtained using a PI-50-1 potentiostat in a three electrode cell with a platinum electrode in benzonitrile solution with $(C_2H_5)_4NClO_4$ electrolyte.

Zincate 6 was synthesized by the method in the study [10].

1-{4-[3,5-Di(trifluoromethyl)benzylthio]-5-methyl-1,3-dithiol-2-ylidene}piperidinium Bromide (2c). 3,5-Di(trifluoromethyl)benzyl bromide (10 mmol) was added to a solution of the mesoionic salt **1** (2.33 g, 10 mmol) in acetone (100 ml) and the mixture was heated to its decolorization. Evaporation of the acetone gave a colorless crystalline product which was used without further purification. Compounds **2a,b,d** were prepared similarly and are oily, hygroscopic materials. The yields of the products are close to quantitative.

5-Methyl-2-piperidino-4-(2,3,5,6-tetrafluorobenzylthio)-1,3-dithiol (3b). Sodium borohydride (12 mmol) was added portionwise to a solution of compound **2b** (10 mmol) in acetonitrile (50 ml), the reaction mixture was diluted with water, and the separated oil was extracted with ether. The ether extracts were dried over sodium sulfate, ether was removed, and the product **3b** was recrystallized from alcohol to give small, colorless, fine needles. Yield 85%.

Compounds 3a,c,d were obtained similarly as oily liquids

1,3-Dithiolium Perchlorates (4a-d) (General Method). An ether solution of compound **3a-d** (1 mmol) was stirred with 70% perchloric acid. The ether was evaporated and the residue was cooled in the fridge. The shining, flaky perchlorate was filtered off and then used without purification. The product yields were 60-70%.

Dimethyldi(arylmethylthio)tetrathiafulvalenes (5a-d) (General Method). Triethylamine was added dropwise to a solution of compound **4a-d** (1 mmol) in dry acetonitrile (3 ml) until precipitation of the product **5a-d** ceased. The latter was then recrystallized from acetonitrile. The compounds are formed as small orange or red needles.

1,3-Dithiol-2-thiones (7a-e) and (9a-d) (General Method). The corresponding fluoro-substituted benzyl or benzoyl chloride (200 mmol) was added to the zincate **6** (3.6 g, 50 mmol) dissolved in acetone (100 ml). The mixture was stirred at room temperature for 1.5 h, the solution was diluted with water, and the yellow crystals were filtered off and recrystallized from alcohol or acetic acid. Yield of thiones 85-95%.

1,3-Dithiol-2-ones (8a,c-e) (General Method). Compound **7a-e** (10 mmol) was heated over 15 min in acetic acid with a small excess of mercuric acetate and the black precipitate of mercuric sulfide was filtered off. The light yellow filtrate was diluted with water, held at room temperature for about 16 h, and the light yellow crystalline product of **8a,c-e** was separated and purified by recrystallization from alcohol.

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