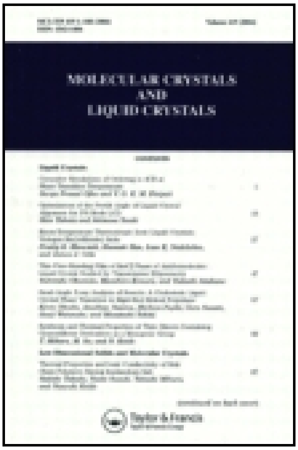

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Dioxo-and Aminooxopyrimido-Fused Tetrathiafulvalenes-Base Compounds for Novel Organic Semiconductors and for Design of Sensors for Recognition of Nucleic Acid Components

Ojars Neilands [a]

[a] Department of Organic Chemistry, Riga Technical University, 14, Azenes Street, LV, 1048, Riga, Latvia

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Dioxo- and Aminooxopyrimido-Fused Tetrathiafulvalenes - Base Compounds for Novel Organic Semiconductors and for Design of Sensors for Recognition of Nucleic Acid Components

OJARS NEILANDS*

Department of Organic Chemistry, Riga Technical University, 14, Azenes Street, LV 1048, Riga, Latvia

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Uracil-fused and isocytosine-fused tetrathiafulvalenes (TTF) are compounds easily synthesised from barbituric acid and its derivatives. The compounds can be easily oxidised, they form cation-radical salts and at the same time intermolecular hydrogen bonds with complementary components enhancing the electroconductivity of crystalline samples. The formation of hydrogen bonds produces changes in the ultraviolet absorption spectra of compounds and in their redox properties: it may be used for the recognition complementary components of nucleic acids. An oligonucleotide containing a TTF group has been synthesised and its redox activity studied.

Keywords: tetrathiafulvalenes; complementary hydrogen bonds; cation-radical salts; organic semiconductors; recognition; oligoribonucleotide

1. INTRODUCTION

TTF **1** (Scheme 1) are electron donating compounds possessing rather low ionisation energies and forming stable cation-radical salts. Electrochemically these compounds are characterised by two reversible redox-transitions (1). Semiconductors, metals and superconductors based on TTF have been obtained in crystalline state (2). TTF condensed with pyrimidine moieties have been first obtained in our laboratory ten years ago (3).

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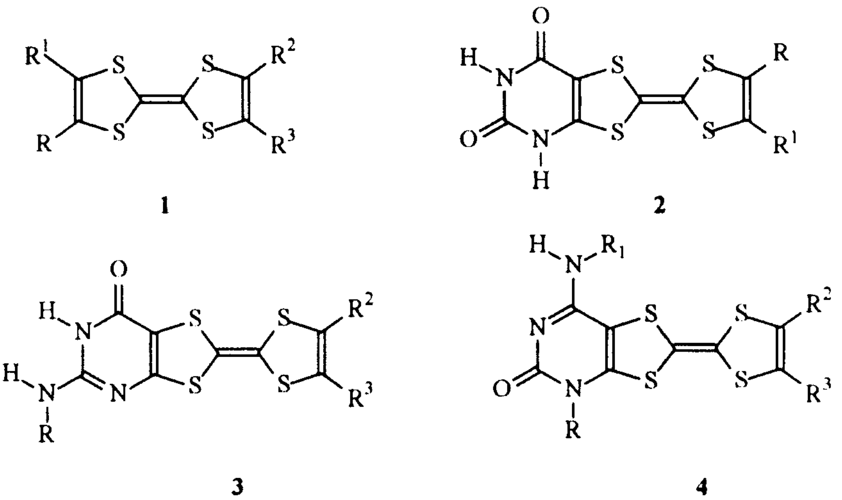
* Corresponding Author.



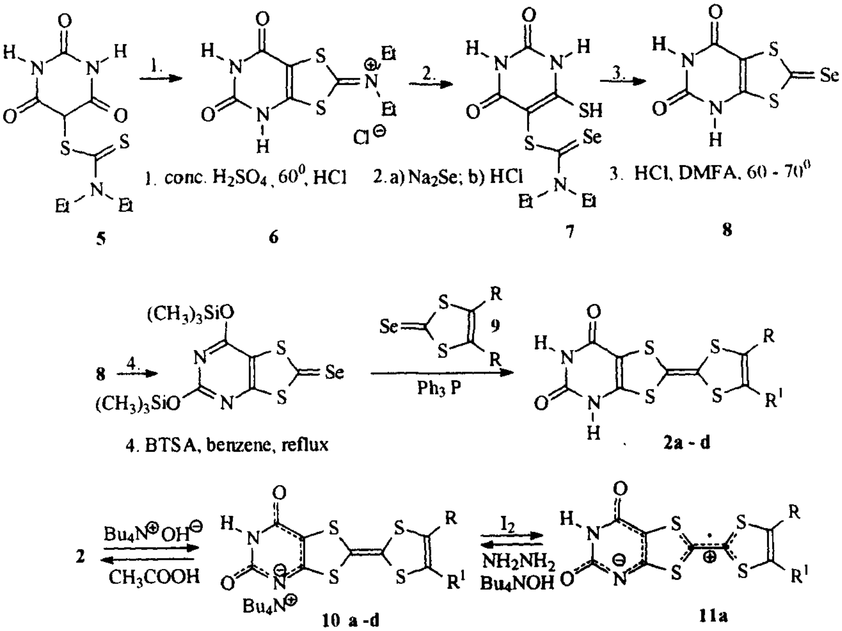
SCHEME 1

Dioxopyrimidotetrathiafulvalenes (uracil-fused TTF) **2** have an important interest as compounds able to form a number of intermolecular hydrogen bonds similarly to nucleic acids by the way of complementary hydrogen bonds and mutual interlinking. At the same time compounds **2** can be easily oxidised and can form cation-radical salts probably possessing semiconductive or metallic properties. Isocytosine-fused TTF **3** or cytosine-condensed tetrathiafulvalenes **4** may present still higher interest, because they may form three complementary hydrogen bonds. As a result of hydrogen bond formation changes in the ultraviolet absorption spectra and in electrochemical properties can be detected.. These changes may be used for the recognition of complementary dioxo- and aminooxoderivatives (which form part of nucleic acids).

The present paper offers some new results in the research concerning the above mentioned TTF as improved synthesis method of TTF **2a** from barbituric acid, butylation and cyanoethylation reactions of **2a**. It also generalises and analyses data previously obtained and discusses perspectives of practical application.

URACIL-FUSED TETRATHIAFULVALENES AND METHODS OF SYNTHESIS OF THEIR DERIVATIVES

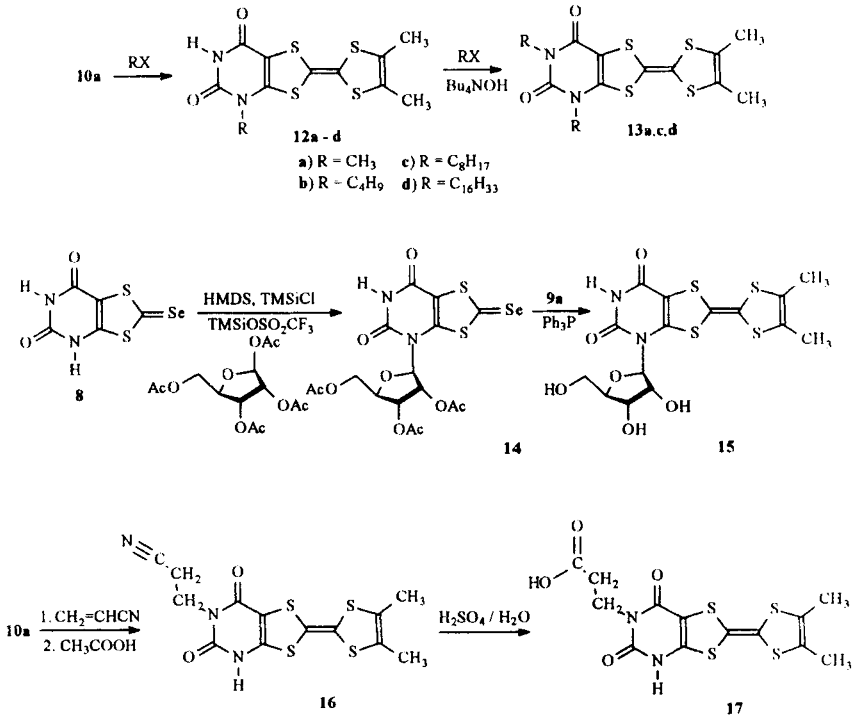
The starting material for synthesis is the easily accessible barbituric acid and its derivatives (Scheme 2). The key compound – 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium chloride **6** can be easily obtained by cyclization of 5-diethylaminothiocarbonylthiobarbituric acid **5** in concentrated sulphuric acid. The synthesis of selone **8** ⁽⁴⁾ has been improved, in which the action of chloride **6** upon the selenide and cyclisation of the isolated 4-thiobarbituric acid derivative **7** is used.



a) R = CH_3 ; R^1 = CH_3 .
b) R = $C_{17}H_{35}$; R^1 = H .
c) R = SCH_3 ; R^1 = SCH_3
d) RR^1 = SCH_2CH_2S

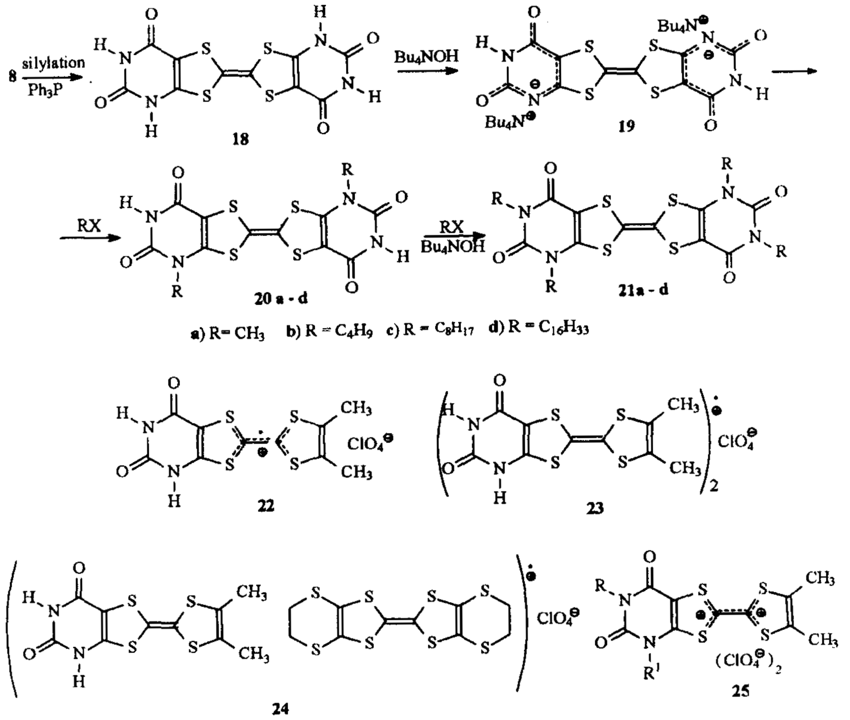
SCHEME 2

The selone **8** is the starting compound for obtaining TTF **2a**. The previously described method ⁽⁵⁾ has been improved. It consists in converting the poorly soluble selone **8** into a trimethysilylderivative by bis-trimethylsilylacetamide (BTSA) with following unsymmetrical coupling into **2**, applying other selones **9** in the presence of triphenylphosphine. The unpurified **2** may be purified in two ways. First, by turning into a tetrabutylammonium salt **10**, and, secondly by oxidising to non-soluble cation-radical betaine **11**, washing off admixtures and reducing back to **2** or **10** with hydrazine hydrate (in the presence of tetrabutylammonium hydroxide). One thus obtains uracil-fused TTF with the following substituents: dimethyl (**2a**), heptadecyl (**2b**), di(methylthio)(**2c**), ethylenedithio (**2d**). The salt **10** may be used for obtaining the derivatives at the nitrogen atom in the uracil ring. Alkylation with halogenoalkanes yields mono- and disubstituted compounds (Scheme 3). 1-N-monosubstituted products **12a-d** are important. A number of them are better soluble than **2a** and can therefore be used in studies with the formation of intermolecular hydrogen bonds. For example, we describe the synthesis of 1-N-butyl-**2** (**12a**) and intermolecular association with formation of complementary hydrogen bonds. The tetraalkyl products **13a-c** do not contain NH bonds, the formation of complementary hydrogen bonds is therefore not possible, but their solubility is better.



SCHEME 3

For obtaining the monosubstituted compounds **2** another path may be taken namely alkylation of selone **8** and coupling through interaction with another selone into TTF. In this way silylation of selone **8** and action upon tetraacetylribose under conditions of nucleoside synthesis yield the first ribonucleoside with added a 1,3-dithiole ring in form of the triacetate **14** (Scheme 3). The latter compound has further been used for the synthesis of ribonucleoside – uridine -fused TTF **15** and of oligoribonucleotides (6,7).



SCHEME 4

The uracil-fused TTF **2** are NH-acids, the ionisation constant pK of 1-NH bond is about 5.0 –5.5. Due to the insolubility of **2a** the ionisation constant could not be measured, but it can be proposed that the pK of **2a** is comparable with the ionisation constant of selone **8**. For selone **8** the pK value in water for the 4-NH group is equal 4.85, but for analogous thione – 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-thione the pK is equal 5.1 (8). It is interesting to note that the pK value for 6-NH bond ionisation of 4-methyl-**8** is equal to 7.6 (8b). We can conclude that ionisation of 1-NH bond in **2a** is preferred over the ionisation of the 3-NH bond. The tetrabutylammonium salt **10a** may be used for obtaining various 1-N-substituted derivatives **2** through interaction with halogenoalkanes. The alkylation reactions may be used for imparting acidic, basic, or amphiphilic properties to compound **2** by changing the substituents. It has proved impossible to introduce a substituent in position 3-N, leaving the 1-N-position free. We have, however, succeeded in observing a peculiar 3-N-substitution in a cyanoethylation reaction by acrylonitrile. The salt **10a**, acting with acrylonitrile yields a 3-(2-cyanoethyl)-**2a** tetrabutylammonium salt, out of which 3-(cyanoethyl)-**2a** (**16**) may be isolated (Scheme 3). Hydrolysis yields the corresponding carboxylic acid **17**, which may be useful in bonding the structure **2** to polymer macromolecules and for grafting to the surfaces of various solids. We explain the peculiar course of the cyanoethylation reaction by possibly easy splitting off of the cyanoethyl group from the 1-N atom in the presence of bases.

Using silylation of selone **8** and action of triphenylphosphine it is possible to achieve a symmetrical coupling and to obtain bis(dioxopyrimido)TTF **18** as finely crystalline yellow-orange substance, which is practically insoluble in water and organic solvents (scheme 4). Through action of tetrabutylammonium hydroxide one may obtain a di-(tetrabutylammonium) salt **19**, which can be alkylated and it is possible to obtain the dialkyl products **20** and the tetralkyl products **21**.

OXIDATION OF URACIL-FUSED TTF AND OBTAINING OF CATION-RADICAL SALTS

Analogously to other TTF (1) compounds **2** are redox-active and they show two reversible redox stages. At the first stage E^1 a cation-radical is formed, and at the second stage E^2 – a dication.

TABLE I Redox behaviour characteristic by Cyclic voltammetry of some TTF (Glassy carbon electrode, reference Ag/AgCl or saturated calomel electrode)

Compound	E_{ox}^{1}/E_{red}^{1} *(V)*		E_{ox}^{2}/E_{red}^{2} *(V)*	
	MeCN	*Other solvent*	*MeCN*	*Other solvent*
		DMFA		DMFA
2a	0.7/0.55	0.62/0.54	0.95/0.85	0.86/0.69
12a	0.7/0.61	0.72/0.63	0.99/0.87	0.96/0.85
13a	0.65/0.58	0.7/0.6	0.97/0,88	0.88/0.78
12b (SCE)	0.56/0.48	MeCN/H_2O 1:1 0.49/0.38	0.92/0.83	MeCN/H_2O 1:1 0.81/0.67
15 (SCE)	0.54/0.47	0.45/0.35	0.87/0.8	0.77/0.61
2d (1N-Me)	unsoluble	DMFA 0.92/0.75	unsoluble	DMFA 1.04
31	0.56/0.43		0.96/0.77	
ET	0.56/0.49		0.80/0.73	
2,6-Dibutoxy-carbonyl-TTF	0.69/0.6		1.02/0.9	

Table I presents redox potential of TTF **2** (reference electrode Ag/AgCl or SCE). As may be seen, TTF **2** oxidises with considerably greater difficulty, as compared to unsubstituted or alkylsubstituted TTF proper and are comparable with the oxidation of bis(ethylenedithio)TTF (ET) or TTF-carboxylic acid. Alkylated compounds **12** and **13** oxidise somewhat more easily. These compounds might be used for obtaining cation-radical salt crystals with the aim of producing organic semiconductors or metals. A number of such experiments are described below. Bis(dioxopyrimido)TTF **18** and its alkylproducts **20** and **21** oxidise with difficulty, their oxidation potentials being comparable with those of TTF dicarboxylic acid derivatives.

On the other hand, tetrabutylammonium salts oxidise easily, their study by cyclic voltammetry (CVA) method is difficult, since the electrode gets coated by a green insoluble layer of oxidation product. Oxidation of the salt **10** by iodine or some other oxidant (phenyliodosyldiacetate), gives an extremely insoluble green powder, which turns out to be an internal salt of a cation radical (betaine) **11**. In this unusual molecule one has simultaneously a positive charge on the TTF part, and an anion centre on the uracil part. In the same time it is a free radical. The unusually low solubility of betaine **11** may be explained by the large lattice energy arising from intermolecular interactions, due to the sum of ionic attraction, lone electron interaction, and intermolecular hydrogen bonding. Owing to the low solubility, this betaine may be used for the purification of compound **2a**. In the presence of reducing agent (hydrazine hydrate) and tetrabutylammonium hydroxyde the betaine is transformed into dioxopyrimido-TTF **2a** tetrabutylammonium salt **10** (Scheme 2). Under the action of strong bases the betaine dissolves slowly with a green tint disappearing in time. Probably in this case an anion of betaine may form, which intramolecularly reduces the cation-radical.

Betaine **11** serves a starting material in obtaining cation-radical salts and corresponding complexes. In the presence of perchloric acid a greenish-black perchlorate **22** may be obtained (Scheme 4). With the aid of ultrasonic techniques, the poorly soluble finely crystalline complexes **23** and **24**, possessing semiconductive properties, may be obtained from betaine **11** and from TTF **2** or bis(ethylenedithio)-TTF in the presence of perchloric acid (9). The electrical properties of compressed samples are presented in table IV.

Cation-radical salts in form of perchlorates may also be obtained from alkylated TTF **12**. The butylsubstituted perchlorate **12b**ClO_4 is a greenish black crystalline substance, which has been characterised spectroscopically.

In the presence of strong oxidants alkylated TTF **12** and **13** produce (Scheme 4) the red dications **25** (10). They can be isolated as red crystallinic perchlorates in the case of methyl- and dimethylderivatives. However, in contact with air moisture the perchlorates are unstable and turn into a green cation radical.

TTF **2a** and their alkylated products are capable to form black charge transfer complexes by interaction with iodine (10). In accordance with constitution of pyrimido-TTF used, the solvent and the quantity of iodine employed complexes with different content of iodine: **2a**.I_3, **12a**.I_3, **12c**.I_4, **12d**.I_4, **13a**.I_4, **13c**.I_6, **13d**.I_6 have been prepared(10). In acetonitrile solution the complexes dissociate partially under the formation of cation-radical salt. These solutions are green and they contain 80% of cation-radical for complex **12a**.I_3 as seen by UV-Vis spectroscopy (10).

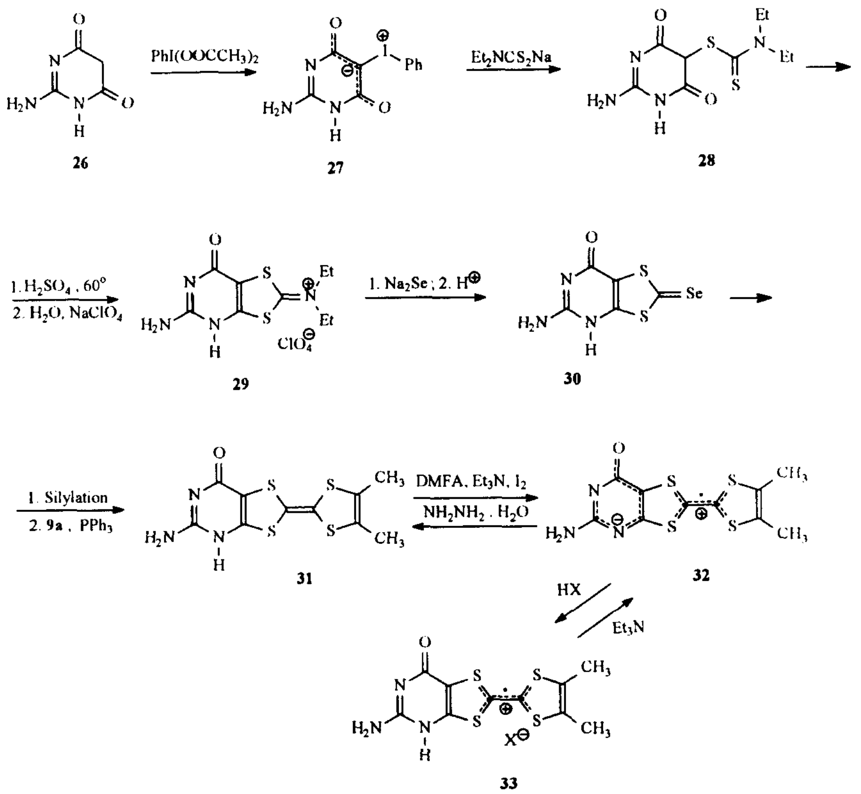
ISOCYTOSINE-FUSED TETRATHIAFULVALENE SYNTHESIS AND PROPERTIES

For the synthesis of isocytosine-condensed of a TTF system (cf. Scheme 5) the starting compound is the 2-iminobarbituric acid derivative 2-amino(1H, 5H)pyrimidine-4,6-dione **26**, which is turned into phenyliodonium betaine **27**and sequentially into diethylaminothiocarbonylthioderivative **28** (11). By cyclisation of **28** 5-amino-7-oxo(6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium perchlorate **29** is being synthesised and on the bases of **29** the key selone **30** is being prepared (11).

Cross coupling reaction of selone **30** with 4,5-dimethyl-1,3-dithiole-2-selone **9a** gave the expected isocytosine-fused TTF **31**. The purification of **31** is achieved by oxidation to the insoluble cation-radical betaine **32**, and its isolation and reduction back to **31**(9,12) with hydrazine hydrate. The TTF **31** obtained forms an orange-yellow finely crystalline powder, poorly soluble in organic solvents. The compound is a weaker NH-acid, as compared to TTF **2a**, its tetrabutylammonium salt hydrolyses easily in water solutions.

The oxidation potential is lower than that of **2a** (Table I), which speaks in favour of the possibility to obtain cation-radical salts. This is, however a difficult process, owing to the low solubility of the compounds. The simplest way is obtaining cation-radical betaine, in which the cation part is located on the tetrathiafulvalene system, but the anion part on the isocytosine system. This reaction is carried out in dimethylformamide solution in the presence of triethylamine with iodine. The betaine **32** obtained forms a greenish-black fine and very insoluble powder, difficult to filtrate. It may be dissolved in acids, forming at low concentration a dark green solution containing cation-radical salts **33**.

Betaine **32** samples in form of compressed tablets reveals peculiar semiconductive properties (9). which will be dealt with lower (Table IV).



SCHEME 5

SPECTROSCOPIC PROPERTIES OF URACIL-FUSED AND ISOCYTOSINE-FUSED TTF

The UV and visible spectra (cf. Table II) show a broad low-intensity absorption band in the 350–500nm region, which causes a yellow-orange colour to the compounds, particularly in the crystalline state. A similar absorption band characterizes a large number of other TTF derivatives containing electron acceptor groups in the molecules, such as e.g. one or more carboxyl groups in form of esters. This absorption may be due to intramolecular charge transfer from the TTF system onto the acceptor group. More intense absorption bands appear in 300nm and 260nm ranges.

A peculiar aspect is presented by the spectra of cation-radicals. Here one observes intensive absorption in the 600–800nm range, which causes green colouring of the substances. An analogous observation may be made in the absorption of tetramethyltetrathiafulvalene cation radical.

TABLE II UV and Visible spectra of some TTF and cation-radicals

Compound	λ_{max} *nm, (ε Lmol^{-1}cm^{-1})*	
	MeCN	*other solvent*
12b	290 (24000), 325 (18600), 395 (3600)	MeCN/H_2O 1:1 292 (25600), 325 (19600), 404 (3600)
15	290 (13600), 324 (11600), 400 (2000)	292 (13600), 324 (12000), 405 (2000)
31	Ethanol	227 (206500, 294 (21900), 393 (3200)
2,6-dibutoxy-carbonyl-TTF	288 (16300), 312 (18200), 432 (4000)	
22	260 (10300), 463 (16000), 702 (4000) (in the presence of $HClO_4$)	
12b ClO_4		CH_2Cl_2 290 (4200), 408 (4000), 468 (5600), 704 (3600)
11a		KBr tablet 409, 720

TABLE III IR spectra of some pyrimido-fused TTF, complexes and cation-radical salts

Compound	ν_{max}*cm^{-1}, interv. 1900–1460 (susp. in paraffin oil)*	ν_{max}*cm^{-1}, int. 3600–2100 (susp. in hexachloro-butadiene)*
2a (orange cryst. from DMFA at temp. <60° C	1680s[a] , 1656vs, 1584m, 1532w	3500w, 3100s, 3000–2920s, 2810m
2a (yellow cryst. from DMFA at temp. > 110° C	1712m, 1642vs, 1574m, 1534w	3150s, 2980s, 2825m
12a	1715, 1632, 1574	3140, 3010, 2875, 2820
13a	1700, 1644, 1592, 1560	2990, 2940, 2880
15	1692s, 1668s, 1572m	3356s, 2920m, 2810m
10a	1620	3100, 3010, 2935, 2800
11a	1650s, 1625s, 1550w	3390, 3090, 2955, 2785
22	1722s, 1675vs, 1560m	3270, 3170, 3050, 2840
2a.I_3	1714, 1670, 1624, 1556	3150, 2920
31	1645, 1605, 1525	3320, 3160, 2960
18	1730, 1715, 1645, 1570	3450, 3050

a. intensity of absorption: vs-very strong, s-strong, m-middle, w-weak

In the double bond region of the IR spectrum, one may observe (cf. Table III) the bands of the uracil system, produced by carbonyl groups, which form strong intermolecular hydrogen bonds in crystalline state. In the 3600–2400cm^{-1} region NH-bond absorption appears, which in their turn participate in the formation of hydrogen bonds. The carbonyl groups of the uracil system lead to absorption in the region 1640–1720cm^{-1}. In the case of TTF **2a** show two absorption motives, 1680 and 1655cm^{-1} or 1700–1715 and 1640cm^{-1} due to different crystalline modifications. A change in the double bond absorption region of betaine **11a**, namely absorption takes place at lower wave numbers, which correspond to changed carbonyl groups in the anion, for example **10a**.

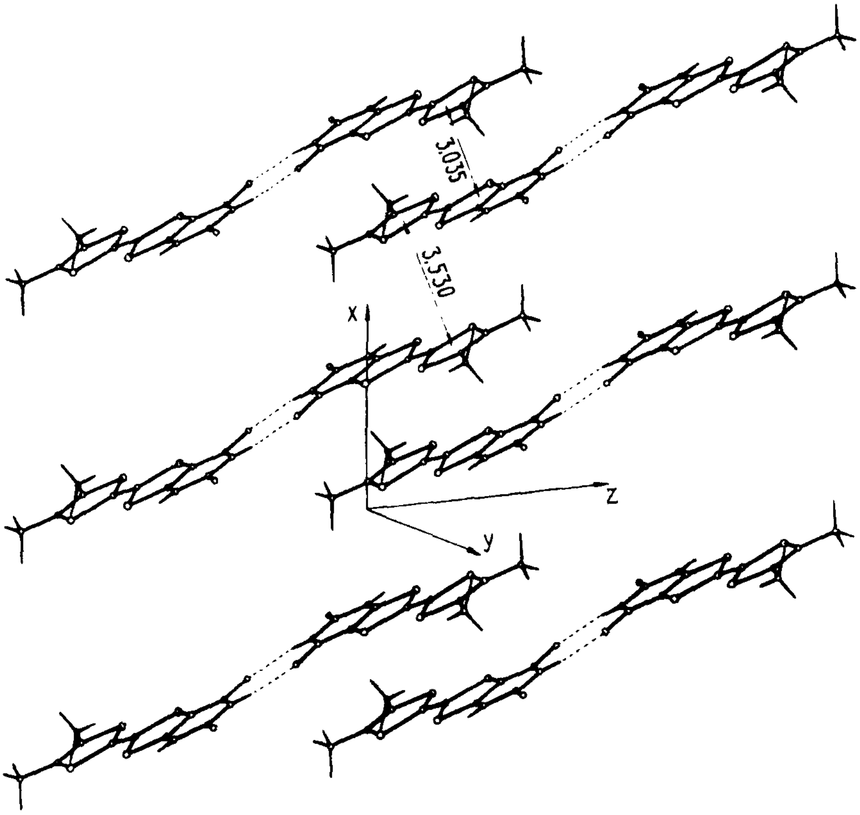


FIGURE 1 Stacking of molecules of **2a** in the crystal

Isotysine condensed TTF **31** absorption in the double bond region reveals one carbonyl group forming intermolecular hydrogen bonding. A good spectrum of the cation-radical betaine **32** is difficult to obtain, owing to diffuse absorption, which may be due to strong intermolecular interaction and relatively high electroconductivity. One may, however, observe that carbonyl absorption of betaine is shifted towards lower wave numbers.

X-RAY STRUCTURE OF URACIL-FUSED TTF

Recrystallisation of TTF **2a** from dimethylformamide-ethanol mixture gives monocrystals containing a dimethylformamide molecule. X-ray measurements confirmed the structure and show that the crystal contains molecular dimers formed with the aid of two hydrogen bonds (13). These dimers are ordered in columns in the crystal, with alternating distances between the planes of the dimers, namely 3.04Å and 3.53Å (cf. Fig. 1).

MASS SPECTRA OF URACIL-FUSED TTF

The 70eV electron ionisation mass spectra of uracil-fused TTF have been studied by accurate mass measurement, metastable ion analysis and collision-induced dissociation(14). Changes in the structure of substituents, both in the TTF moiety and on the 1-N atom of uracil, cause important differences in the fragmentation scheme. The position of alkyl substituents in the uracil ring is unambiguously confirmed. The fragmentation of dimethylsubstituted TTF **2a** characterizes by loss of HNCO, but fragmentation of ethylenedithiosustituted TTF **2d** involves the loss of ethylene from dihydrodithiine ring.

ELECTROPHYSICAL MEASUREMENTS

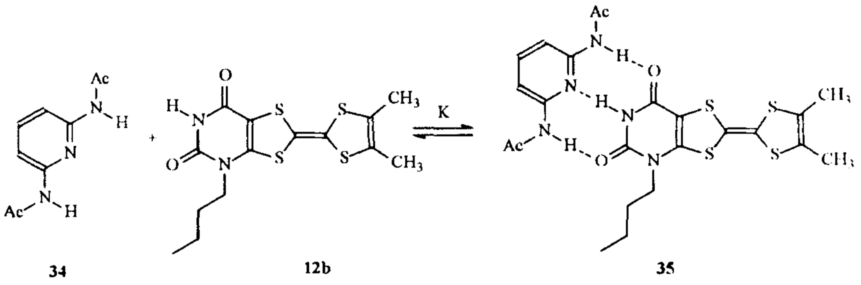
Electroconductivity was measured for a number of samples in compressed tablet form, as well as current-voltage dependencies at various temperatures (9). Semiconductive properties have been observed with various activation energies for different compounds (cf. Table IV). An unusually high electroconductivity or low activation energy have been found for cation-radical betaine **32** and complex **24**. The electrical measurements of the novel cation-radical salts and betaines in compressed tablets showed an unexpectedly low resistivity and semiconducting behaviour with small activation energies. We could presume to explain the unexpectedly high conductivity of cation-radical betaines as being due to strong intermolecular interaction through hydrogen bonds. Our investigations allows to predict the possibility of synthesising novel, highly conducting materials on the bases of oxo(amino)pyrimido-TTF cation-radical salts and betaines, especially in the case of the double salts of type **23** and **24**.

TABLE IV Electrophysical measurements data of some pyrimido-fused TTF cation-radical salts and betaines (compressed tablets of diameter 1.2 cm and thickness 0.075–0.165 cm)

Compound	*Specific resistivity* ρ Ω*cm*		*Activation energy* E_a *eV*		
	297 K	*Other T*	*260–290 K*	*220–260 K*	*Other T*
22	$3.8 \cdot 10^8$		0.2		
23	38	147 K $8 \cdot 10^3$			150–195 K 0.13
24	48		0.05		203–240 K 0.08
11a	840	$5.8 \cdot 10^5$	0.22	0.30	200–223 K 0.49
32	5 – 10	183 K 10^3		0.2	
2a.I_3	$3 \cdot 10^6$	163 K $2.4 \cdot 10^{11}$	0.23	0.6	

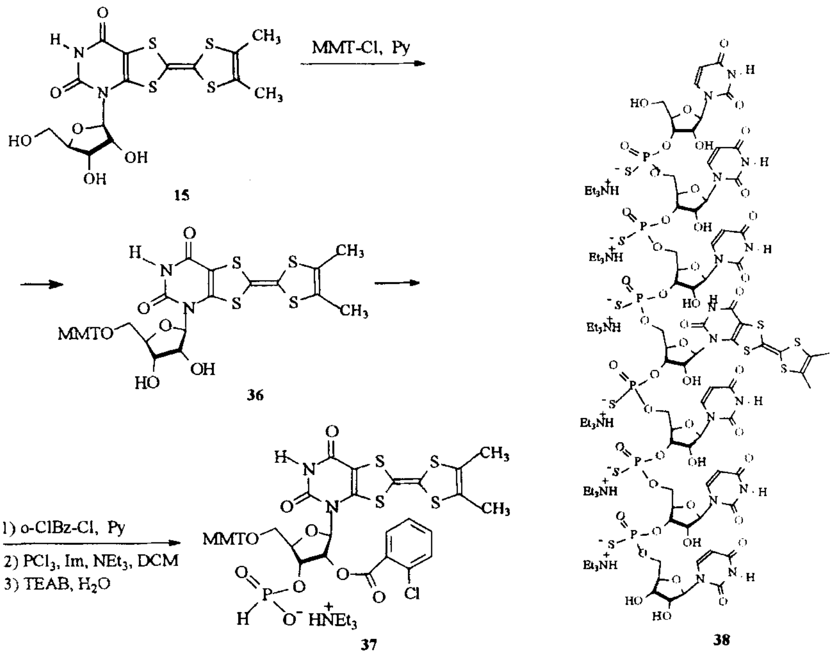
INTERMOLECULAR ASSOCIATION WITH FORMATION OF COMPLEMENTARY HYDROGEN BONDS AND ITS EFFECT ON SPECTROSCOPIC AND ELECTROCHEMICAL PROPERTIES

In order to study intermolecular associations, the relatively good soluble alkyl-product was chosen with a butyl group **12b** and as the complementary component – 2,6-di(acetylamino)-pyridine **34** (Scheme 6). Association was studied in dichloromethane solution, applying UV and visible spectra, as well as cyclic voltammetric measurements (15). A H-bond complex **35** of these hydrogen bonds was also obtained in crystalline state.



SCHEME 6

Adding **34** to a solution of compound **12b** a ca. 10nm bathochromic shift of maximum at 406nm was observed in the spectrum. This shift was the larger, the more **34** was added. Owing to the limited solubility of compound **34** it was not possible to achieve saturation, at which almost all **12b** would be converted into the complex **35**. Therefore the formation constants of the complex could be determined only by fitting the experimental points. The estimated formation constant of the complex K=1000–1050mol^{-1}. Applying CVA method, it was possible to determine an increase in oxidation potential with increase in **34** content, the difference reaching a value of 0.03 V. The value of K = 1500 mol^{-1} was estimated from electrochemical data (15). The data presented show that the formation constant of the complex is similar to those for complex formation of other uracil derivatives with **34** (16). Spectroscopic and electrochemical changes indicate that in the course of the formation of complex **35** an increase in electron acceptor properties of the uracil fragment occurs. This causes bathochromic shift of the intramolecular electron transfer band and inhibits electrochemical oxidation.



SCHEME 7

The above example suggests the conclusion that by formation of complementary hydrogen bonding changes in the UV and visible spectra, as well as in oxidation potentials will be produced in solution of other dioxo- and aminooxopyririmido-TTF. These changes could be used for recognition of various nucleosides and nucleotides in solution. To this purpose it would be necessary to synthesise various pyrimido-fused TTF and to introduce them into molecules of oligonucleotides. This oligonucleotide in solutions or deposition this on the electrode surface, makes it possible to expect spectroscopic or electrochemical changes in the presence of complementary nucleobases. We are presenting an example of such a synthesis.

SYNTHESIS OF REDOX-ACTIVE HEPTARIBONUCLEOTIDE CONTAINING TTF MOIETY

The starting material is the ribonucleoside **15**, in fact ribosylated TTF **2a** (Scheme 3). In multistage changes *via* protected by monomethoxytrityl group MMT ribonucleoside **36** a oligoribonucleotide H-phosphonate synthesis block **37** (Scheme 7) (7) has been synthesised. Further an automatic nucleotide synthesator for solid phase oligosynthesis has been applied, and for the first time heptaribonucleotide phosphothioate **38** with nucleotide sequence 5′-UsUsUs(U-TTF)sUsUsU-3′ has been obtained. That is one TTF block has been implanted between six uridine residues (7). This oligoribonucleotide is redox-active which oxidation potential is lower as for ribonucleoside **15**.

2. EXPERIMENTAL PART

SYNTHESIS OF 5,7-DIOXO(4H,6H)-1,3-DITHIOLO[4,5-d] PYRIMIDINE-2-SELONE 8

5-(diethylaminothiocarbonylthio)barbituric acid **5** monohydrate (17), 3.81g (13mmol) has been dissolved in conc. sulfuric acid, 12mL and stirred and warmed at temperature 60–65°C for 1h. The solution has been cooled and added to crushed ice, 25g, under stirring and cooling conc. hydrochloric acid, 24mL and acetone, 120mL has ben added. In 1h the colourless crystals of 5,7-dioxo(4H,6H)-1,3-dithiolo[4,5-d]pyrimidine-2-diethylimmonium chloride **6** were filtered up, washed with acetone and dried. The yield was 3.4g (89%), temp. of decomp. > 250°C. IR spectra, cm^{-1}: 1710, 1685, 1605, 1559. PMR, in DMSO-d^6, δ: 1.35 t, 6H; 3.92 q, 4H, 11.9 broad, 1H.

Selenium powder, 0.8g (10.1mmol) has been suspended in water, 50mL, and under stirring and flushing by argone time of time sodium tetrahydridoborate, 0.45g, 11.8mmol) has been added to dissolvation of selenium. A solution of chloride **6**, 2.94g (10mmol) in water, 30mL, containing sodium hydroxide, 0.4g (10mmol) has been added to above-prepared selenide solution, stirred for 30min, acetic acid, 3mL added, filtered and filtrate acidified with conc. hydrochloric acid, 5mL. Precipitate **7** after 10min has been filtered up, washed with water, methanol, diethylether and air dried for 2h. The yield of compound **7** was 3–3.1g (90%) and this substance immediately has been used for cyclisation.

A mixture DMFA, 34mL and conc. hydrochloric acid, 17mL has been warmed to temperature 60°C and under stirring the compound **7**, 3g added. The mixture turned in red and has been stirred at temperature 75–80°C for 20min. After cooling the mixture has been diluted with water, 100mL and red selone **8** filtered up, washed with water and dried. The yield of raw selone was 1.75–1.85g (67%). For purification 1.8g of selone is being dissolved in DMFA, 30mL at temperature 60°C, filtered up from small quantity of selenium and filtrate diluted with warm water, 60mL at temperature 60°C. After cooling in 2h the dark brown crystals **8** has been filtered up, the yield was 1.5g (55%).

IR spectra, cm^{-1}: 1700, 1640, 1535. PMR, DMSO-d^6 + $CDCl_3$, δ: 11.4, 12.1.

SYNTHESIS OF DIMETHYL[2,4-DIOXO(1H,3H)PYRIMIDO] TETRATHIAFULVALENE, TETRABUTYLAMMONIUM SALT 10a

5,7-Dioxo-1,3-dithiolo[4,5-d]pyrimidine-2-selone **8**, 0.265g (1mmol) has been suspended in dry benzene, 5mL, bis-(trimethylsilyl)-acetamide, 0.5mL (2.2mmol) has been added and mixture heated under reflux for 1h, selone **8** dissolved. The red solution has been cooled (25°C), and a solution of 4,5-dimethyl-1,3-dithiole-2-selone **9**, 0.4 g (2mmol) in warm benzene, 5mL has been added to the silylated selone solution. Triphenylphosphine, 1.57g (6mmol) has been dissolved in benzene, 10mL and added to solution of selones mixture. The orange red solution has been kept at room temperature for 24h. Solution, which is turned in dark brown, has been filtered up and to the solution has been added ethanol, 2mL. After 2h the red fine precipitate has been filtered up and thoroughly washed with ethanol till colourless liquid flows down, and dried at 80–90°C. The yield of row TTF **2a** was 0.28g.

To mixture of acetonitrile, 14mL and 10% water solution of tetrabutyl-ammonium hydroxide, 3.3mL, above synthesized row TTF **2a**, 0.28g has been added, and the mixture has been heated under reflux for 15min till dissolvation of **2a**. Hot water, 42mL and charcoal has been added to this solution, heated under reflux for 5 min and filtered off. After keeping for 5h at 0–5°C the brownish yellow crystals of salt **10a** have been filtered up, washed with water and dried. The yield of salt **10a** was 0.3g (54%), m.p.199–201°C (decomp.)$^{(3)}$.

SYNTHESIS OF DIMETHYL-[1-BUTYL-2,4-DIOXO(1H,3H) PYRIMIDO]TETRATHIAFULVALENE 12b

Tetrabutylammonium salt **10a**, 0.558g (1mmol) has been dissolved in acetonitrile, 40mL under reflux and 1-butyliodide, 0.4mL (3.5mmol) added. The mixture has been refluxed for 1 h. After cooling the butyl product has been filtered off, the yield was 0.3g (80%). Recrystallisation from acetonitrile, 300mL gave 0.25g of pure **12b**, m.p. 256–257°C (decomp.).

^{1}H-NMR ($CDCl_3$, d): 0.91 (t, 3H, CH_3-CH_2), 1.44 (m, 4H, CH_2), 1.96 (s, 6H, CH_3), 3.69 (t, 2H. CH_2-N), 11.67 (s, 1H, H-N)(15).

SYNTHESIS OF DIMETHYL-[3-(2-CYANOETHYL)-2,4-DIOXO(1H,3H) PYRIMIDO] TETRATHIAFULVALENE 16

Tetrabutylammonium salt **10b**, 0.4g (0.72mmol), ethanol, 1.6mL and acrylonitrile, 4mL have been heated under reflux till the starting compound is being reacted up completely (5–6h), checking by TLH on silica gel, eluent ethanol/triethylamine 4:1 (before analysis the sample should be acidified by acetic acid, red precipitate filtered off and analysed). The reaction mixture has been diluted with ethanol, 16mL, filtered and acidified with acetic acid, 2mL. The red precipitate has been filtered up and recrystallised from mixture of dimethylformamide, 10mL and acetonitrile, 25mL.The yield of pure cyanoethylation product as red crystals was 0.22g (83%), temp. decomp. >270°C. IR spectra (λ_{max} cm^{-1}): 1710, 1618, 1578, 1534; 3225, 3160, 2990, 2925, 2254). ^{1}H-NMR (DMSO-d^6, δ): 1.97 (s, 6H, CH_3), 2.82 (t, 2H, CH_2-CN), 4.0 (t, 2H, CH_2-N).

SYNTHESIS OF DIMETHYL-[3-(2-CARBOXYETHYL)-2,4-DIOXO (1H,3H)PYRIMIDO]-TETRATHIAFULVALENE 17

Compound **16**, 0.2g (0.54mmol) has been dissolved in a mixture of conc. sulfuric acid, 2mL and water, 2mL by heating at 80–90°C and kept at this temperature for 2h. The yellow brown solution has been diluted with water, 40mL and the extra fine precipitate has been filtered off and washed with water. The obtained yellow reddish clay like filter cake has been dissolved in a mixture of ethanol, 20mL and dimethylformamide, 15mL by reflux, filtered and kept at 0–5°C for 24h. The hydrolysis product **17** crystallises as light red fine leaflets, yield 0.1 g (48%). ^{1}H-NMR (DMSO-d^6. δ): 1.93 (s, 6H, CH_3), 2.5 (t, CH_2-COOH), 3.96 (t, 2H, CH_2-N), 12.25 (broad, 2H, H-N and H-O).

3. CONCLUSIONS

Various methods of synthesis have been tried and various tetrathiafulvalene derivatives have been synthesized, containing fused uracil and isocytosine systems in the molecule, thus bestowing on TTF derivatives the capacity of forming complementary hydrogen bonds. On the other hand, dioxo- and aminoooxopyrimidine systems thus become redox-active; may form cation-radical salts and intermolecular hydrogen bonds, and additionally assist in obtaining materials with high conductivity. It has been shown that the compounds studied may form peculiar cation-radical salts – cation-radical betaines possessing singular high conductivity, on behalf of the formation of intermolecular hydrogen bonding. It has been shown that aminooxopyrimido-TTF systems, by forming intermolecular hydrogen bonds, change absorption spectra and oxidation potentials. This phenomenon may be used for the recognition of various pyrimidine and purine derivatives contained in nucleic acids, or oligonucleotides. We have succeeded in synthesis of such oligoribonucleotide, which contains a TTF group in the molecule, thus indicating a way towards creating sensors for recognition of nucleic acid parts. The dioxo- and aminooxopyrimido-fused TTF systems may be useful in two ways. First, as starting material for the design of charge transfer complexes and radical salts by using the formation of intermolecular hydrogen bonds, and secondly as a component for sensor construction.

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