Chemistry of Heterocyclic Compounds, Vol. 32, No. 1, 1996

PYRIMIDOTETRATHIAFULVALENES.

3.* SYNTHESIS AND PROPERTIES OF CATION-RADICAL SALTS, CATION-RADICAL BETAINES, AND COMPLEXES OF DIMETHYL[2,4-DIOXO(1H,3H)PYRIMIDO]TETRATHIAFULVALENE AND ITS N-ALKYL SUBSTITUTED DERIVATIVES WITH IODINE

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The reaction of dimethyl[2,4-dioxo(1H,3H)-pyrimido]tetrathiafulvalene and its N-alkyl derivatives with iodine leads to the formation of complexes with various numbers of iodine atoms. Depending on the conditions, the betaine of the cation-radical of dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene or a complex of the latter with dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene is formed by the oxidation of the pyrimidotetrathiafulvalene. The cation-radical perchlorates are formed on carrying out the oxidation of dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene and its N-methyl derivatives in the presence of perchloric acid. The preparation of the cation-radical salts is usually linked with the reaction of the cation-radical betaine with acids.

The tetrathiafulvalenes, their cation radical-salts and various complexes occupy a significant place among organic conductors [2]. Crystal structure is important among the factors determining their electrical conducting properties. Consequently our interest is linked with derivatives of dioxopyrimidotetrathiafulvalene which may form stable intermolecular hydrogen bonds [3]. The subject of investigation in the present work was dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene and its N-alkyl derivatives [3]. The aim of the present work was the preparation of complexes with iodine and the preparation of cation-radical perchlorates on oxidation of tetrathiafulvalene with various oxidizing agents.

Compound (Ia) and its N-alkyl derivatives (Ib)-(Ig) are extremely poorly soluble, consequently the preparation of complexes from them is linked with some difficulty. A solvent mixture of sulfolane and acetonitrile was successful for obtaining the complex of iodine with compound (Ia). The complex (IIa) of iodine with compound (Ia) is more soluble than the tetrathiafulvalene (Ia) itself and was obtained by treating a hot suspension of compound (Ia) in a sulfolane – acetonitrile mixture with an excess of iodine. Compound (IIa) was isolated with an iodine content $x > 3$ but after crystallization from the same mixture the complex (IIa) had an iodine content $x = 3$.

The formation of complex (IIa) was also observed on maintaining compound (Ia) in an atmosphere containing iodine vapor.

The N-alkylated compounds (Ib)-(Ig) are more soluble and their complexes with iodine were obtained in acetonitrile solution or in an acetonitrile – chloroform mixture. The complexes obtained have various compositions, the number of iodine atoms in them depends on the size of the substituent on the nitrogen atoms. Thus the N-methyl- and N,N'-dimethyl derivatives (Ib,e) formed complexes containing I_3 with a tenfold excess of iodine in $CH_3CN-CHCl_3$ solution, and this composition did not change on crystallization.

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*For part 2 see [1].

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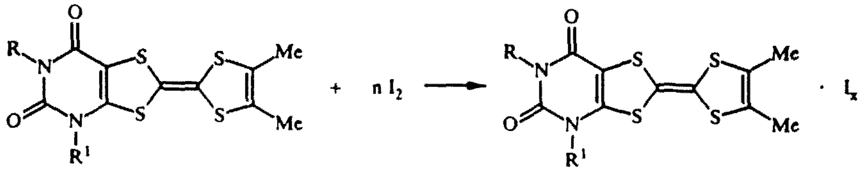


Ia-g IIa-g

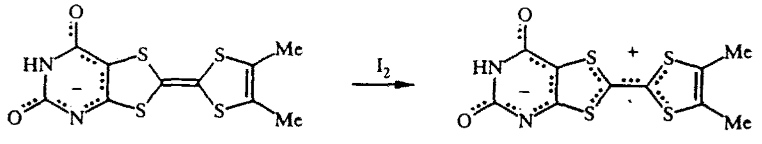
I, II a $R = R^1 = H$, $x = 3$; b $R = H$, $R^1 = Me$, $x = 3$; c $R = H$, $R^1 = C_8H_{17}$, $x = 4$;
d $R = H$, $R^1 = C_{16}H_{33}$, $x = 4$; e $R = R^1 = Me$, $x = 4$; f $R = R^1 = C_8H_{17}$, $x = 6$;
g $R = R^1 = C_{16}H_{33}$, $x = 6$

The complexes of monoalkyl derivatives (Ic) and (Id) with the more voluminous substituents (C_8H_{17}, $C_{16}H_{33}$) had the composition $(I)\cdot I_4$. It was established in the case of the fulvalene (Ic) that the complex with this number of iodine atoms was formed both with a large excess of iodine and with a two-fold excess but in lower yield. The complex with 4 atoms of iodine was also obtained on electrochemical oxidation of compound (Ic) in the presence of Et_4NI_3.

A twenty-fold excess of iodine was required to obtain complexes of iodine with tetrafulvalenes (If) and (Ig) containing large substituents at both nitrogen atoms. The complexes (IIIf) and (IIIg) were more soluble and less stable. The unrecrystallized reaction products contained ~6 atoms of iodine per molecule of compound (I), but on recrystallization from CH_3CN lost approximately half of the iodine and the substance obtained was a mixture containing free tetrathiafulvene as well.

The IR spectra and the electronic absorption spectra of the complexes (II) in CH_3CN solution are given in Table 1.

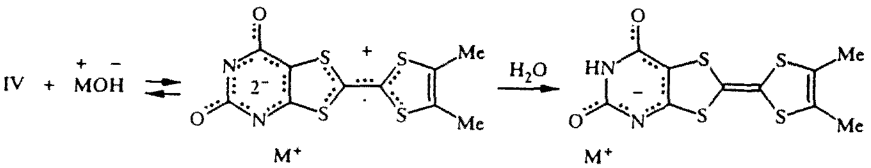
The reaction of compound (Ia) with iodine in the presence of bases (triethylamine) in DMF solution or the reaction of the tetrabutylammonium salt of tetrathiafulvalene (Ia) with iodine in CH_3CN or in DMF solution leads to the formation of a dark green finely crystalline insoluble precipitate. In our opinion anion (Ia) is oxidized in this reaction and an unusual cation-radical internal salt, the betaine (IV), which contains a cation-radical of tetrathiafulvalene and an anion from the uracil portion, is formed.



III.a,b IV

IIIa X = $HNEt_3$; b X = Bu_4N

It is possible to use oxidizing agents other than iodine, e.g., tetracyanoquinodimethane. The betaine (IV) is practically insoluble in water and organic solvents but is capable of dissolving in the presence of alkali with the formation of unstable green solutions. The green coloration rapidly disappears and a salt of the initial compound (Ia) is formed. Probably the reduction of the cation-radical occurs due to the electron-donating action of the dianion of the uracil portion.

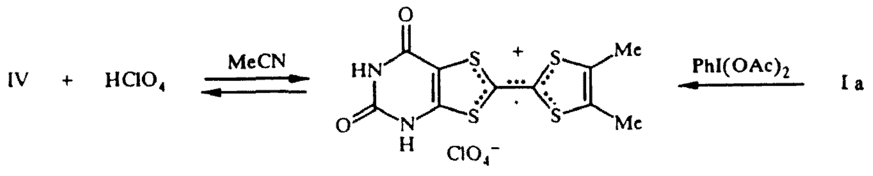


The betaine structure of compound (IV) was confirmed by the IR spectra in which intense absorption was observed at 1622 and 1650, characteristic of the dioxopyrimidine anion, and the absorption of carbonyl groups at 1680-1710 cm^{-1} disappeared. The electronic absorption spectra and the reflections for solid betaine (IV) confirmed the presence of a cation-radical (absorption at 720 nm). According to electron paramagnetic resonance data, the content of free radicals in crystalline compound (IV) was only 3.4%. Evidently the betaine (IV) exists mainly as a dimer. In addition, grinding the crystals of (IV) finely with KBr changes the shape of the EPR spectrum (see Fig. 1), which may be explained by the presence in compound (IV) of radical pairs disappearing on dilution with KBr. Using the value for the broadening of the EPR spectra D = 0.9 mT observed for the initial (IV), according to the equation from [5]:

$$r = \sqrt[3]{\frac{2780}{D}}$$

it is possible to estimate the distance r between the radicals in the pairs, which in our case is 14.5 Å.

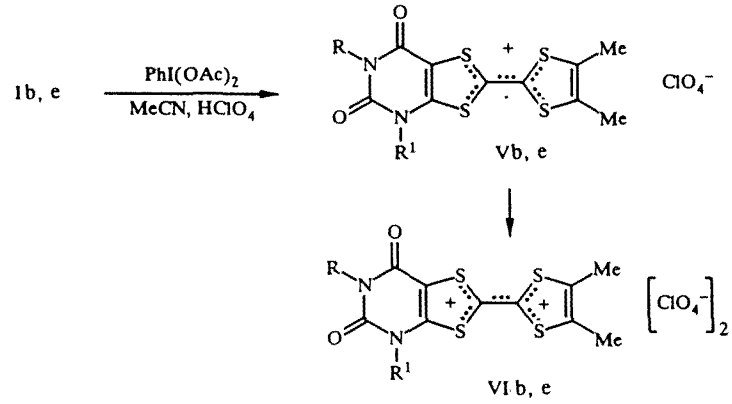
The betaine (IV) reacts with acids (such as perchloric) with the formation of cation-radical salts [such as (Va) perchlorate].



V a

We also succeeded in developing a procedure for the oxidation of the same tetrathiafulvalene (Ia) to the cation-radical salt. It was possible to use (diacetoxyiodo)benzene or potassium hexacyanoferrate (III) as oxidizing agent. The (Va) perchlorate formed dark green crystals, which decomposed explosively on melting, and were poorly soluble in organic solvents and water, giving dark green solutions. Partial formation of the insoluble betaine (IV) occurred on heating solutions, probably as a result of the ionization of (Va) perchlorate as an NH acid. Heating aqueous and alcoholic solutions caused disappearance of the green coloration and the formation of yellow-brown solutions and a precipitate, probably due to reduction of the cation-radical to compound (Ia) and other irreversible changes occurring in parallel in the tetrathiafulvalene system.

Also obtained were the perchlorates (Vb) and (Ve) of the N-methyl and N,N′-dimethyl derivatives of compounds (Ib) and (Ie) by direct oxidation with $PhI(OAc)_2$ or $K_3Fe(CN)_6$ in the presence of perchloric acid in CH_3CN solution.



V, VIbR = H, R^1 = Me; e R = R^1 = Me

The perchlorates were crystals almost black in color, but perchlorate (Ve) was violet. Their solutions were dark green.

An unusual phenomenon was observed when obtaining the perchlorates (V), viz., the generation of a red color which changed to green. We are inclined to explain this by further oxidation in the excess of oxidizing agent and the formation of the red-colored diperchlorates (VI). They may be precipitated as red crystals from solution in CH_3CN with diethyl ether, but we did not succeed in isolating them in the pure state. They were extremely readily reduced to the salts (V) and were only stable in solution in the presence of an excess of oxidizing agent. The UV spectrum of compound (VI) was characterized by absorption at 360 and 485 nm.

Cyclic voltamperometry of perchlorates (Va), (Vb), and (Ve) in acetonitrile showed two reversible oxidation stages (Table 2). Evidently the cation-radical system of the compounds is very readily reduced at a cathode, and the values obtained for E_{ox} and E_{red} correspond to those of the same tetrathiafulvalenes (Ia), (Ib), and (Ie) (Table 2). The possibility therefore arose of determining the E_{ox} and E_{red} of these compounds in acetonitrile, which was unsuccessful by the direct route [4] due to their poor solubility.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Empirical formula	IR spectra, cm^{-1}, in the range 1500-1800 and 2400-3600 cm^{-1}	UV spectra, λ_{max}, nm (ε), in CH_3CN	Yield, %
IIa	$C_{10}H_8I_3N_2O_2S_4$	1558 (40), 1626 (63), 1670 (55), 1714 (53), 2940, 3150	291 (39000), 361 (8950), 455 (8100), 718 (3600)[*]	40
IIb	$C_{11}H_{10}I_3N_2O_2S_4$	1558 (51), 1694 (70), 2854, 2930, 3163, 3443	292 (56000), 362 (29000), 435 sh (8800), 460 sh (8700), 718 (4600)	50
IIc	$C_{18}H_{24}I_4N_2O_2S_4$	1543 (40), 1652 sh (45), 1684 (67), 2860, 2920, 2980	291 (41000), 362 (19500), 442 (7250), 466 (7500), 525 sh (2000), 718 (4400)	60
IId	$C_{26}H_{40}I_4N_2O_2S_4$	1543 (43), 1652 (48), 1681 (86), 2865, 2920, 2950	292 (39000), 361 (20100), 440 sh (3100), 465 sh (3200), 530 sh (2000), 719 (2900)	66
IIл	$C_{12}H_{12}I_3N_2O_2S_4$	1570 (72), 1650 (79), 1726 (57), 2860, 2930	290 (56300), 362 (25700), 440 (5130), 462 (5250), 530 sh (2080), 718 (2570)	64
IIf	$C_{26}H_{40}I_6N_2O_2S_4$	1568 (56), 1594 (57), 1658 (91), 1692 (74), 1714 (65), 2860, 2920, 2960	293 (72400), 362 (35000), 470 sh (9000), 718 (4900)	35
IIg	$C_{42}H_{72}I_6N_2O_2S_4$	1538 (46), 1668 (74), 1682 (58), 1724 (78), 2860, 2930	291 (72600), 362 (36000), 460 sh (10000), 720 (5300)	30
IV	$C_{10}H_7N_2O_2S_4$	1550 (35), 1624 (76), 1650 (75), 2800, 2850, 2950, 3100	409 (1350), 720 (1250)[†]	
Va	$C_{10}H_8ClN_2O_6S_4$	1560 (62), 1676 (85), 1722 (77), 1750 (68), 2840, 3050, 3170, 3270	260 (10300), 463 (16000), 702 (4000)[‡]	50
Vb	$C_{11}H_{10}ClN_2O_6S_4$	1552 (42), 1672 (72), 1714 (70), 1736 sh (60), 2924, 3120	294 (65000), 345 (16700), 401 (8400), 445 (8600), 468 (9200), 717 (5600)	35
Vd	$C_{12}H_{12}ClN_2O_6S_4$	1520 (60), 1578 (65), 1652 (76), 1712 (76)	294 (6220), 334 (4200), 5405 (5000), 445 (7650), 469 (9210), 719 (5900)	35
VII		1542 (41), 1580 (50), 1622 (85), 1658 (69), 1722 (78), 2870, 2924, 3140, 3450	288 (7800), 401 (5200), 719 (3520)[†]	73

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[*] Spectrum was taken in sulfolane–acetonitrile, 2 : 1.

[†] Absorption spectrum in a KBr disk.

[‡] Spectrum was taken in acetonitrile solution containing $HClO_4$.

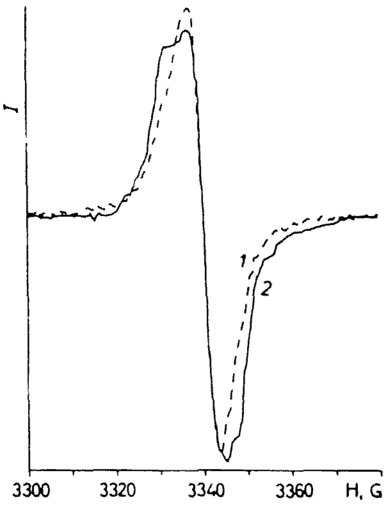


Fig. 1. EPR spectra of the betaine cation-radical dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene (IV): 1) diluted with KBr; 2) in the pure state.

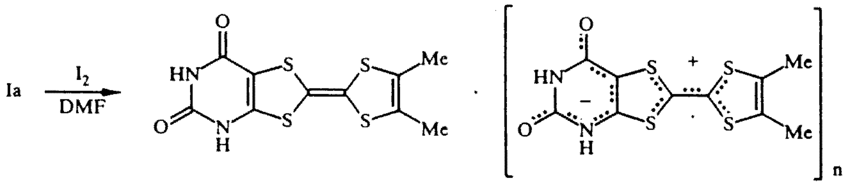
TABLE 2. Data of Cyclic Voltamperometry of Compounds (Ia), (Ib), and (Ie)

Compound	E_1^{ox} (V)	E_2^{ox} (V)	E_1^{red} (V)	E_2^{red} (V)
Ia	0,72	0,94	0,57	0,84 [1]
Iб	0,67	1,00	0,60	0,87
Iд	0,70	0,92	0,58	0,88

Calculations on the electron paramagnetic resonance spectrum of perchlorate (Va) showed that due to the bulky ClO_4 anion the molecules of the cation-radicals were further separated from one another than in the betaine (IV), and the proportion of free radicals was 43 ± 2%.

The characteristic absorption of the cation-radical system was observed at 720 nm in the UV spectra of perchlorates (V) (Table 1). This absorption band is also present for all the complexes of the tetrathiafulvalenes with iodine (IIa-g) in acetonile solution. The proportion of cation-radicals in the complexes of tetrathiafulvalene with iodine was determined by comparing the values of ε for the absorption at 720 nm of the perchlorates and of the iodine complexes of the analogous compounds (Ib) and (Ie). For complexes (IIb) and (IIe) in acetonitrile solution this was 80 and 40% respectively. This indicates that there is an equilibrium between the unoxidized and oxidized forms.

Dimethylformamide (DMF) was the most effective solvent for obtaining solutions of compound (Ia), however, it was not possible to isolate the perchlorates (V) in DMF. This solvent may be used successfully to obtain the betaine (IV) from salts of (Ia), but reaction of the same tetrathiafulvalene (Ia) with iodine in DMF solution gave an unexpected result, viz., precipitation of a finely crystalline, difficultly soluble green substance which was not betaine (IV). Judging by data of IR spectra and diffuse reflection spectra, the substance is a complex of betaine (IV) and fulvalene (Ia) where n = 4-6. The absorption maxima in the IR spectra at 1338 [betaine (IV)] and 1712 cm^{-1} [tetrathiafulvalene (Ia)] were used for an approximate assessment of the composition.



Complex (VII) was also formed on electrochemical oxidation of compound (Ia) in a DMF–CH_3CN (3:1) mixture.

EXPERIMENTAL

The IR spectra were taken on a Specord IR 75 instrument for suspensions in paraffin oil and in hexachlorobutadiene. Electronic absorption spectra were taken on a Specord UV-vis. Voltamperograms were taken with a Pye 50-1 potentiostat in the three-electrode mode. The operating electrode was glass–graphite, the reference electrode saturated Ag/AgCl, base electrolyte was Bu_4NClO_4 (0.1 M), and potential scanning rate 200 mV/sec.

Complex of Dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene with Iodine (IIa). The fulvalene (Ia) (0.32 g, 1 mmole) was suspended in sulfolane (23 ml). The mixture was heated to 80°C, acetonitrile (13 ml) containing iodine (1 g, 8 mmole) was added, and the mixture boiled for 1 min. The solution was filtered hot. A black solid containing 48.5% iodine remained on the filter. Complex (IIa) (0.35 g, 50%) precipitated from the filtrate on cooling. Acetonitrile (10 ml) was added to the filtrate and further (IIa) (0.03 g) was obtained after 24 h at 0°C. Complex (IIa) (0.38 g) was crystallized from a mixture of sulfolane (12 ml) and acetonitrile (6 ml) giving complex (IIa) (0.28 g) as fine black needles. Found, %: C 17.30, H 0.82, N 3.93, S 16.63, I 53.15. $C_{10}H_8I_3N_2O_2S_4$. Calculated, %: C 17.23, H 1.16, N 4.02, S 18.40, I 54.61.

Complex of Dimethyl[N-octyl-2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene with Iodine (IIc). A. Acetonitrile (20 ml) containing iodine (0.5 g, 4 mmole) was added to a hot solution of fulvalene (Ic) (0.17 g, 0.4 mmole) in chloroform (15 ml). The precipitated black solid (0.35 g) was filtered off and washed with acetonitrile. Complex (IIc) (0.2 g) was obtained as fine black needles after crystallization from acetonitrile. Found, %: C 23.69, H 2.35, N 3.05, S 13.40, I 55.02. $C_{18}H_{24}I_4N_2O_2S_4$. Calculated, %: C 23.09, H 2.58, N 2.99, S 13.70, I 54.22.

B. Fulvalene (Ic) (0.02 g, 0.05 mmole) and Et_4NI_3 (0.13 g, 0.25 mmole) were dissolved in a mixture (20 ml) of acetonitrile–chloroform (1:1). Electrocrystallization was carried out on a Pt anode at constant current (10 μA) at room temperature. Black crystals of complex (IIc) (0.015 g: 20%) had formed after 72 h.

Complexes (IIb), (IId), and (IIe) were obtained similarly by method A.

(IIb). Found, %: C 18.30, H 1.47, N 3.78, S 17.75, I 51.6. $C_{11}H_{10}I_3N_2O_2S_4$. Calculated, %: C 18.58, H 1.42, N 3.94, S 18.03, I 53.53.

(IId). Found, %: C 29.60, H 3.89, N 2.51, S 11.97, I 49.20. $C_{26}H_{40}I_4N_2O_2S_4$. Calculated, %: C 29.78, H 3.85, N 2.67, S 12.23, I 48.42.

(IIe). Found, %: C 20.14, H 1.28, N 3.86, S 17.72, I 52.07. $C_{12}H_{12}I_3N_2O_2S_4$. Calculated, %: C 19.87, H 1.67, N 3.86, S 17.69, I 52.49.

Complex of [N,N'-Dioctyl-2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene with Iodine (IIf). Acetonitrile (10 ml) containing iodine (1 g, 8 mmole) was added to a hot (70-75°C) solution of fulvalene (If) (0.2 g, 0.4 mmole) in acetonitrile (20 ml) and the solution filtered. After cooling, black crystals (0.19 g, 36%) containing 57% iodine were isolated from the filtrate. A mixture of substances with an iodine content of 35% was obtained after crystallization from acetonitrile.

Complex (IIg) was obtained analogously.

Betaine of Cation-Radical Dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene (IV). Acetonitrile (10 ml) containing iodine (3 mmole) was added to a solution of the tetrabutylammonium salt (IIIb) (0.28 g, 0.5 mmole) in acetonitrile (50 ml). The precipitate was filtered off and washed with acetonitrile. Betaine (IV) (0.14 g) was obtained as a fine green powder with mp > 300°C. Found, %: C 38.37, H 2.20, N 8.74, S 40.51. $C_{10}H_7N_2O_2S_4$. Calculated, %: C 38.08, H 2.24, N 8.88, S 40.66.

Cation-Radical Dimethyl[2,4-dioxo(1H,3H)tetrathiafulvalene Perchlorate (Va). **A**. The fulvalene (Ia) (0.3 g, 1 mmole) was suspended in acetonitrile (100 ml) and $HClO_4-CH_3COOH$ (5 ml), obtained from 55% $HClO_4$ (1.2 ml) and acetic anhydride (4.2 ml), was added. A solution of (diacetoxyiodo)benzene (0.15 g, 0.5 mmole) in acetonitrile (3 ml) was added in small portions with stirring during ~20 min. The solution was heated and filtered hot. Salt (Va) (0.32 g) was isolated from the filtrate on cooling as fine dark green needles.

B. Betaine (IV) (0.31 g, 1 mmole) was suspended in acetonitrile (100 ml) and anhydrous $HClO_4$ (10.3 ml, 10 mmole) in acetic acid [prepared from 55% $HClO_4$ (2.4 ml) and acetic anhydride (8.4 ml)] was added in small portions. The resulting green solution was heated to boiling, filtered hot, and left for 24 h at 0°C. Dark green crystals of (Va) (0.2 g) were obtained. Found, %: C 28.69, H 1.86, N 6.53, S 30.74. $C_{10}H_8ClN_2O_6S_4$. Calculated, %: C 28.88, H 1.94, N 6.74, S 30.84, Cl 8.53.

Cation-Radical Dimethyl[1-N-methyl-2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene Perchlorate (Vb). A mixture (0.14 ml) of perchloric acid and acetic acid containing 0.25 mmole perchloric acid was added to a suspension of fulvalene (Ib) (0.06 g, 0.2 mmole) in acetonitrile (5 ml). A solution of (diacetoxyiodo) benzene (0.03 g, 0.1 mmole) in acetonitrile (2 ml) was added dropwise. The fulvalene (Ib) dissolved with the formation of a green solution. The mixture was heated to boiling and filtered. Black crystals of salt (Vb) (0.03 g) were obtained from the filtrate. Found, %: C 30.62, H 2.27, N 6.40, S 29.70, Cl 8.70. $C_{11}H_{10}ClN_2O_6S_4$. Calculated, %: C 30.73, H 2.34, N 6.52, S 29.83, Cl 8.25.

Cation-Radical Dimethyl[1,3-N,N'-dimethyl-2,3-dioxo(1H,3H)pyrimido]tetrathiafulvalene Perchlorate (Ve). A solution of perchloric acid (0.15 ml, 0.27 mmole) in acetic acid (prepared from 55% perchloric acid and acetic anhydride) was added to a suspension of fulvalene (Ie) (0.07 g, 0.2 mmole) in acetonitrile (5 ml). (Diacetoxyiodo)benzene (0.02 g, 0.06 mmole) in acetonitrile (1 ml) was added in small portions to the solution. The solution acquired a red color initially and then became greenish brown. The mixture was heated to boiling and filtered. After cooling violet crystals of (Ve) (0.03 g) were obtained. Found, %: C 32.17, H 2.49, N 6.29, S 28.62, Cl 7.86. $C_{12}H_{12}ClN_2O_6S_4$. Calculated, %: C 32.46, H 2.72, N 6.31, S 28.89, Cl 7.99.

Complex of the Betaine Cation-Radical of Dimethyl[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene with Dimethyl-[2,4-dioxo(1H,3H)pyrimido]tetrathiafulvalene (VII). **A**. The fulvalene (Ia) (0.31 g, 1 mmole) was dissolved in dimethylformamide (32 ml) by heating and a solution (6 ml) of acetonitrile–dimethylformamide (1:2) containing iodine (6 mmole) was added at 80°C. The precipitated green solid was filtered off, washed with DMF, and then with acetonitrile. Complex (VII) (0.23 g) of mp > 250°C was obtained.

B. Fulvalene (Ia) (0.06 g) and Bu_4NClO_4 (0.2 g) in DMF (15 ml) and acetonitrile (5 ml) were loaded into an electrolysis cell with Pt electrodes. Electrocrystallization was carried out at room temperature at constant current (10 μA). After 48 h the dark green complex (VII) (0.01 g) had formed on the anode. Found, %: C 37.96, H 2.10, N 8.71, S 40.60.

REFERENCES

1. O. Ya. Neiland, V. Zh. Tilika, and A. S. Edzhinya, Khim. Geterotsikl. Soedin., No. 9, 1285 (1994).
2. M. R. Bryce, Chem. Soc. Rev., **20**, 355 (1991).
3. O. Neilands, S. Belyakov, V. Tilika, and A. Edzina, J. Chem. Soc., Chem. Commun., No. 3, 325 (1995).
4. O. Ya. Neiland, V. Zh. Tilika, and A. S. Edzhinya, Khim. Geterotsikl. Soedin., No. 8, 1122 (1992).
5. S. Ya. Pshezhotskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. I. Tupikov, Electron Paramagnetic Resonance (EPR) of Free Radicals in Radiation Chemistry [in Russian], Khimiya, Moscow (1972), p. 447.
6. A. P. Ivanov, Optics of Dispersing Media [in Russian], Nauka i Tekhnika, Minsk (1969), p. 98.