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Some New Reactions and Properties of Xanthane Hydride (5-Amino-1,2,4-dithiazole-3-thione)

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Abstract—Aminomethylation of xanthane hydride (5-amino-1,2,4-dithiazole-3-thione) with the RNH_2–HCHO system has resulted in the formation of the derivatives of new heterocyclic system (3,7-dihydro-5*H*-[1,2,4]-dithiazolo[4,3-*a*][1,3,5]triazine) in low yields. The reaction of xanthane hydride with dicyandiamide has led to thioammeline [4,6-diamino-1,3,5-triazine-2(5*H*)-thione]. Some practically important properties of xanthane hydride and its derivatives have been investigated. Xanthane hydride has efficiently exhibited carbon steel corrosion in neutral aqueous media. The prepared compounds have not exhibited growth-regulating or antidote activity to herbicide 2,4-D.

Keywords: xanthane hydride, 5*H*-[1,2,4]dithiazolo[4,3-*a*][1,3,5]triazin-3-thione, dicyandiamide, thioammeline, Mannich reaction

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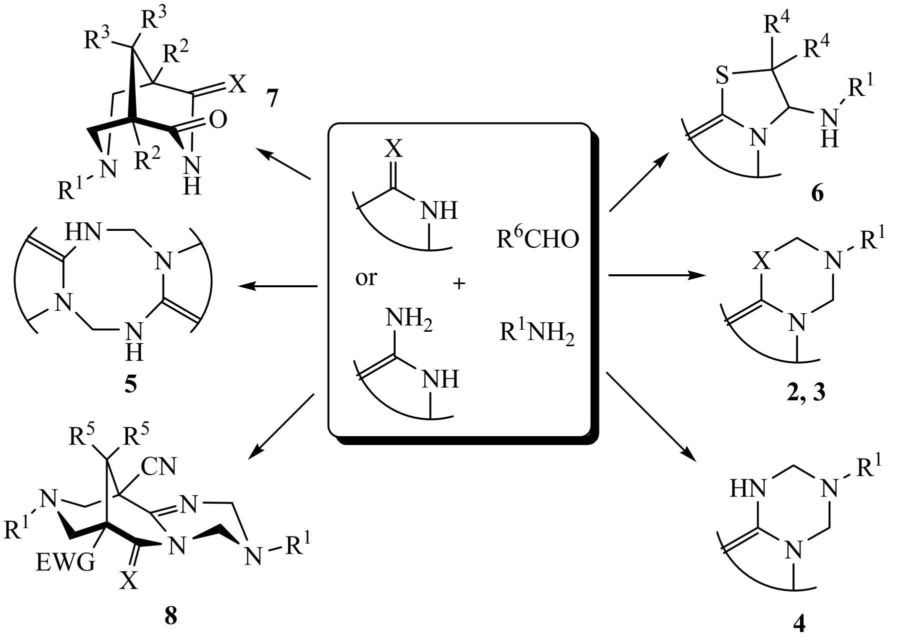
Xanthane hydride (isoperthiocyanic acid) **1** is the first organic compound synthesized by F. Wöhler (1821) from inorganic compounds (mercury thiocyanate and HCl) [1] 7 years before the classical synthesis of urea from ammonium cyanate. The actual structure of xanthane hydride as 5-amino-3*H*-1,2,4-dithiazole-3-thione has been confirmed by means of X-ray diffraction analysis [2, 3], IR [4], and NMR spectroscopy [5, 6] as well as mass spectrometry [7]. Chemical properties of xanthane hydride have been briefly described in reviews [8, 9]. Xanthane hydride has relatively wide range of applications as sulfur transfer agent in rubber vulcanization [8], sulfurization of oligonucleotides [10–12], and synthesis of 1,2,4-triazole and 1,2,4-dithiazole derivatives [9]. However, a lot of reactions and properties of 5-amino-3*H*-1,2,4-dithiazole-3-thione have not been studied.

We have earlier found that aminomethylation of azole and azine substrates containing mercapto (thioxo), selenoxo, or amino group in the position 2 with respect to heteroatom results in the formation of fused deriva-tives of 1,3,5-thiadizine **2** [12–15], 1,3,5-selenadiazine **3** [16], 1,3,5-triazine **4** [17], 1,3,5,7-tetrazocine **5** [18], thiazole **6** [19], 3,7-diazabicyclo [3.3.1]nonane (bispidine) **7** [20–22], or polycyclic structures **8** [23–25], depending on the reaction conditions and the substrate structure (Scheme 1).

Xanthane hydride **1** is a convenient substrate for double aminomethylation and can be transformed into derivatives of certain above-mentioned heterocyclic systems due to the presence of the functional fragment $H_2N–C=N–C=S$. We have failed to find any information on the application of xanthane hydride **1** in the Mannich reaction. Here some new transformations and properties of this compound are reported.

Xanthane hydride was aminomethylated at heating with primary amines and HCHO with the formation of

Scheme 1.

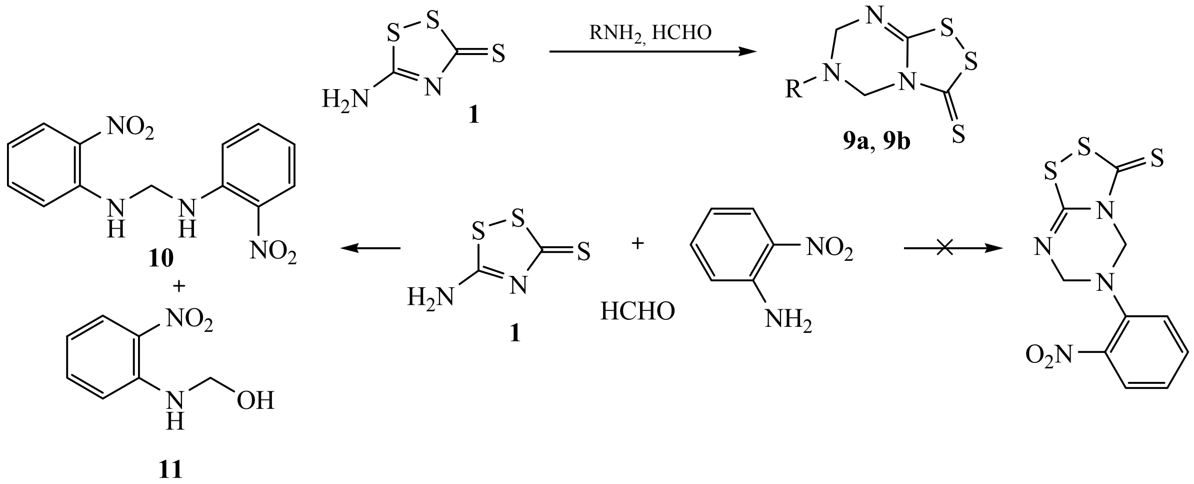


X = S (**2**), Se (**3**).

the derivatives of new heterocyclic system {6,7-dihydro-5*H*-[1,2,4]dithiazolo[4,3-*a*][1,3,5]triazin-3(5*H*)-thione} **9a**, **9b** (Scheme 2) in low yields (9–18%). The amines containing acceptor substituents did not react this way. In the case of 2-nitroaniline, a mixture of diamine **10** and [(2-nitrophenyl)amino]methanol **11** in the ~3 : 4 ratio (^{1}H NMR spectroscopy data) was formed instead of the products of aminomethylation of compound **1**. We suppose that the low yield of compounds **9a**, **9b** was caused by the prominent degradation of xanthane hydride under the action of nucleophilic agents (amines or water) under the reaction conditions; thus, sulfur was isolated as by product in all cases. The structure of compounds **9a**, **9b** was confirmed using IR as well as ^{1}H and ^{13}C spectroscopy data.

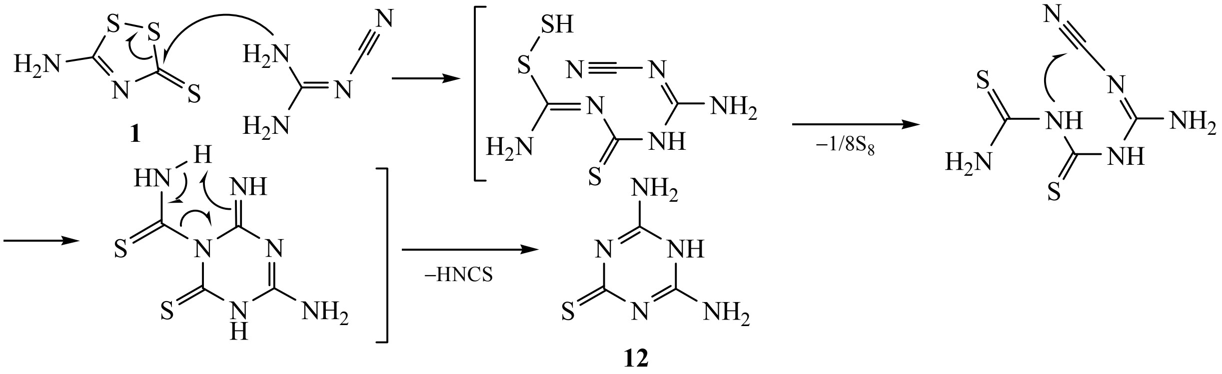
Xanthane hydride **1** can easily react with various *N*-nucleophiles with the formation of diverse aminolysis products [8]. We found that compound **1** easily reacted with dicyandiamide (*N*-cyanoguanidine) with the

Scheme 2.

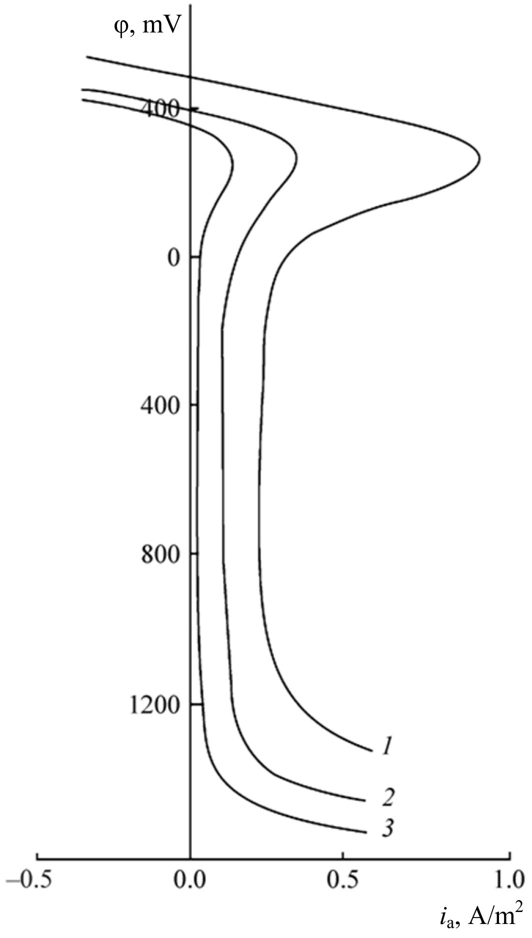


R = CH$_2$Ph (**a**), Ph (**b**).

Scheme 3.



formation of sulfur and a colorless crystalline substance soluble in alkali. This substance was identified as thioammeline [4,6-diamino-1,3,5-triazine-2(5*H*)-thione] **12** using the data of IR and ^{1}H, ^{13}C NMR spectroscopy as well as HPLC–MS (Scheme 3). The suggested mechanism included *N*-thiocarbamoylation of dicyandiamide, elimination of sulfur, and further cyclization.



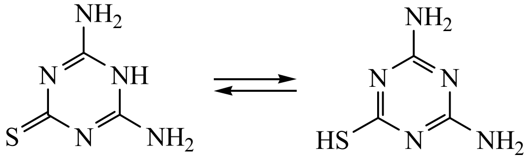
Anodic polarization curves of steel 20 samples in borate buffer solution (pH = 7.4) with natural aeration: (*1*) without inhibitor addition (reference experiment); (*2*) and (*3*) with the addition of 0.5 and 1 g/L of compound **1**, respectively.

The first synthesis of thioammeline **12** was performed by Rathke via the reaction of ammonium thiocyanate with dicyanodiamide [26]. The procedure was then improved [27], and alternative synthetic routes involving dicyanodiamide and thiourea [28] or 2-chloro-1,3,5-triazine-4,6-diamine and sodium thiosulfate [29] were developed. The identity of the prepared compound **12** and thioammeline was confirmed by a set of analytical data. The peak with *m/z* 144 [*M* + 1] was observed in the HPLC–MS spectra of the product. The ^{1}H NMR spectrum contained signals of amino groups (6.81 and 7.38 ppm) and a broad signal of the NH proton (11.20 ppm). The ^{13}C NMR spectrum contained only two signals (160.4 and 181.9 ppm); this fact confirmed high-symmetric structure of the molecule. The IR spectrum of compound **12** was identical to that of thioammeline [27].

The structures of 2-thione [27, 29] or 2-thiol forms [27] were attributed to thioammeline. We compared the experimental IR spectra with the simulated ones. The harmonic frequencies were simulated using hybrid functional PBE0 (PBE1PBE) [30, 31] with the Dunning basis cc-pVTZ [32, 33] implemented in ORCA software package [34, 35]. The comparation of the calculated frequencies with the experimental ones was performed taking into account the scaling factors [0.9565 for high (>1000 cm^{-1}) and 0.9747 for low (<1000 cm^{-1}) frequencies] [36]. The results (Table 1) indicated that the compound existed as the thione tautomer **12A**.

Xanthane hydride as inhibitor of corrosion. Xanthane hydride **1** can inhibit corrosion of carbon

Table 1. The comparison of the major absorption bands in the experimental and simulated IR spectra of tautomeric thioxo (**12A**) and thiol (**12B**) forms of thioammeline



12A **12B**

Assignment	ν_{exp}, cm^{-1}		ν_{calc}, cm^{-1}	
	[36]	this study	**12A**	**12B**
δ(C–N)	780	778.2 s	768.7818	744.2961 821.5857
δ(S–H)	–	–	–	887.8997
C–S	–	–	–	922.4454
δ(C–N)	950	942.1	914.1989 966.4258	974.2979
C–S, δ(N–H)	–	–	–	1015.0388
C=S	–	1068.5	1083.5091	–
δ(C–N)	1200 s	1191.0 s	1210.0512	1126.9059
C=S	1300 s	1292.3 s	1273.3292	–
C–N	1485	1471.6	1432.6034	1311.5159 1418.7865
δ(NH, NH_2)	1535 s	1520.8 s	1540.6128 1562.3504	1453.2111
δ(NH, NH_2)	1595 s	1584.5 s 1625.9 s	1607.4372	1575.4810 1596.6174
C=N	1700 s	1682.8 s	1682.3082	1542.5745
S–H	–	–	–	2604.9828
$\nu_s(NH_2)$	3150	3116.8	3440.2494	3493.8833
NH	3370	3347.3	3482.6286	–
$\nu_{as}(NH_2)$	3410	3387.8	3549.6846	3627.9369 3628.7546

steel in neutral aqueous media. The anodic polarization curve in the background solution (without addition of compound **1**) was characteristic of steel corrosion in neutral media with oxygen depolarization (see figure). The characteristic parts could be seen: active dissolution, passivation (from the onset to complete passivation), passivated state, and transpassivation. Potential of complete passivation was about 0 mV, the transpassivation potential was about 1200 mV, current density of the passivation onset was 0.91 A/m^2, current density in the passivated state was 0.23 A/m^2. Addition of 0.5 g/L of compound **1** as the potassium salt solution led to decrease in the current density of the passivation onset to 0.36 A/m^2, the current density in the passivated state was down to 0.09 A/m^2. Potential of complete passivation was not significantly changed, and the transpassivation potential was increased to 1340 mV. The addition of 1 g/L of xanthane hydride led to further decrease in the current density of the passivation onset to 0.12 A/m^2, the current density in

Table 2. The results of the investigation of antidote activity of compounds **1** and **9a** with respect to herbicide 2,4-D[a]

Compound	Organ	Control, L_k	Reference 2,4-D		Concentration of solutions, %							
			L_r	HA	10^{-2}		10^{-3}		10^{-4}		10^{-5}	
					L_a	A_r	L_a	A_r	L_a	A_r	L_a	A_r
1	Stem	85	47	45	41	87	43	81	39	80	41	87
	Root	169	63	73	57	90	50	79	55	87	58	92
9a	Stem	70	38	46	42	110	39	103	35	92	33	87
	Root	141	53	62	54	102	47	89	35	66	41	77

[a] L_k is an organ length (mm) in the control group of seedlings; L_e is an organ length (mm) in the reference group of seedlings; L_a is an organ length (mm) in the group of seedlings treated with herbicide and antidote; HA, herbicide action, %; HA = $[(L_k - L_r)/L_r]\times 100\%$; A_r – antidote effect, %; $A_r = (L_a/L_r)\times 100\%$.

the passivated state being as low as 0.02 A/m^2. The potential of complete passivation was slightly decreased (from –20 to –50 mV), and the transpassivation potential was increased to 1450 mV, which caused significant extension of the passivated state region.

Hence, xanthane hydride was found to be relatively efficient inhibitor of carbon steel corrosion in neutral aqueous media with oxygen depolarization. Corrosion inhibiting coefficient which was estimated as the ratio between anodic current densities in the pristine and the passivated state was 11.5; that was a relatively high value. The mechanism of inhibiting action of xanthane hydride was not investigated in detail in this study and will be considered elsewhere.

Xanthane hydride and its derivatives as herbicide antidotes and plant growth regulators. The prepared compounds were studied as antidote of herbicide 2,4-D and plant growth regulators. The investigation of efficiency of those compounds as 2,4-D antidotes was carried out using sunflower seedlings in All-Russian Research Institute of Biological Protection of Plants (Krasnodar) via original roll technique [37]. Germinated sunflower seeds with length of embryo root 2–4 mm were placed in a solution of herbicide 2,4-D (2,4-dichlorophenoxyacetic acid) with concentration 10^{-3}% for 1 h to obtain 40–60% inhibition of hypocotyl growth. After the herbicide treatment, the were washed with water and placed into a solution of the tested compounds (concentration 10^{-2}, 10^{-3}, 10^{-4}, or 10^{-5}%) as the "herbicide + antidote" samples. After 1 h, the seeds were washed with water and placed on paper stripes (size 10×75 cm, 20 seeds per stripe), the stripes were rolled and placed into a beaker containing 50 mL of water. The "herbicide" sample (reference) seeds were kept in 2,4-D solution with concentration 10^{-3}% for 1 h and then in water for 1 h. The "control" sample seeds were kept in water for 2 h. Temperature of the solutions was 28°C. The seeds were then incubated for 3 days in a thermostat at 28°C. Each experiment was performed in triplicate; 20 seeds were used in each experiment. The protecting (antidote) effect was determined from the increase in hypocotyl and root length in the "herbicide + antidote" sample relative to the "reference" one. Statistical processing of the experimental data was performed using the Student *t*-test at *p* 0.95.

According to the data given in Table 2, xanthane hydride **1** did not act as a 2,4-D antidote under the experimental conditions and exhibited depressant action on seedlings. Among the aminomethylation products, only compound **9a** exhibited moderate antidote activity (antidote affect A_r was 110% at concentration 10^{-2}%), but the antidote effect was weakened (being changed to the suppressing activity) with the decrease in concentration.

In the investigation of the growth regulating activity of the prepared compounds (concentration 10^{-2}–10^{-5}%) on sunflower seedlings (Table 3), the effect was determined from the increase in the stalk and root length in the group of treated seedlings relative to the "control" group. Statistical processing of the experimental data was performed using the Student *t*-test at *p* 0.95. According to the data given in Table 3, xanthane hydride **1** did not exhibit growth regulating activity. Compound **9a** exhibited the best results of the investigated compounds: its growth regulating

Table 3. The results of the investigation of growth regulating activity of compounds **1** and **9a**[a]

Compound	Organ	Control L_k	Concentration, %							
			10^{-2}		10^{-3}		10^{-4}		10^{-5}	
			L_a	A	L_a	A	L_a	A	L_a	A
1	Stem	88	62	70	67	76	69	78	74	88
	Root	183	111	61	135	74	135	87	134	73
9a	Stem	69	73	106	68	99	76	110	77	112
	Root	140	138	99	126	90	139	99	144	103

[a] L_k is an organ length (mm) in the control group of seedlings; L_a is an organ length (mm) in the group of treated seedlings; A is the growth regulating effect, %. $A = (L_a/L_r)\times100\%$.

activity was about 110–112% at concentration range 10^{-4}–10^{-5}%.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance III HD 400MHz and an Agilent 400/54 [400 (^{1}H) and 101 MHz (^{13}C)] spectrometers in DMSO-d_6. The signals of TMS and residual signals of the solvent were used as reference. The IR spectra were registered using a Bruker Vertex 70 spectrophotometer equipped with an ATR unit. Elemental analysis (C, H, N) was performed using a Carlo Erba 1106 instrument. HPLC–MS/MS analysis was carried out using a Thermo TSQ Quantum Access Max instrument, triple quadrupole, Thermo Ultimate 3000 liquid chromatograph. Melting points were measured using a Koeffler apparatus. The purity of the obtained compounds was controlled by means of TLC on Sorbfil-A plates, eluting with an acetone–hexane 1 : 1 mixture and developing with iodine vapor or $KMnO_4$ solution in aqueous H_2SO_4.

5-Amino-1,2,4-dithiazole-3-thione (xanthane hydride, 1) was prepared via a method adopted from [38]. 35.5 g (0.466 mmol) of ammonium thiocyanate was dissolved in 20 mL of water in a 200 mL beaker. Then 100 mL (0.537 mmol) of 18% HCl (*d* 1.088 g/cm^3) was added to the solution under stirring. The crystals formed after 6 h were filtered off, carefully washed with warm water from the ammonium chloride impurities, and dried. Yield 8.1 g (35%), yellow needle-shaped crystals, mp 200–202°C. IR spectrum, ν, cm^{-1}: 3199.8, 3005.9 (N–H), 1621.1 (C=N), 1300.0, 1082.0 (C=S). ^{1}H NMR spectrum, δ, ppm: 9.66 s (1H, NH_2), 9.79 s (1H, NH_2). ^{13}C NMR spectrum, δ_C, ppm: 183.6 (C^5), 208.8 (C=S).

6-Benzyl-6,7-dihydro-5*H*-[1,2,4]dithiazolo[4,3-*a*]-[1,3,5]triazine-3-thione (9a). A mixture of benzylamine (0.25 mL, 2.4 mmol), compound **1** (0.36 g, 2.4 mmol), 1.5 mL of DMF, 21% aqueous solution of HCHO (0.65 mL, 4.8 mmol, *d* 1.062 g/mL), and 10 mL of EtOH was refluxed until the formation of precipitate (2–3 min). The obtained crude product containing dithiazolotriazine **9a**, initial compound **1**, and sulfur was washed with BuOH and purified using flash chromatography on silica gel (60 μm, eluent—hot EtOAc). After ethyl acetate was distilled off, the reaction product was isolated as light-yellow crystals. Yield 18%, mp 115°C. IR spectrum, ν, cm^{-1}: 3028, 2983, 2942 (C–H), 1599, 1568 (C=N, C=C), 1475 (N–C=S I), 1290, 1272 (N–C=S II), 1021 (C=S). ^{1}H NMR spectrum, δ, ppm: 3.87 s (2H, $C\underline{H_2}Ph$), 4.86 br. s (2H, NCH_2N), 5.16 br. s (2H, NCH_2N), 7.33–7.34 m ($5H_{Ar}$). ^{13}C NMR spectrum, δ_C, ppm: 53.4 (CH_2N), 54.3 (CH_2N), 67.1 (CH_2N), 127.4 (C^4, Ph), 128.1 ($C^{2,6}$, Ph), 128.6 ($C^{3,5}$, Ph), 135.6 (C^1, Ph), 154.3 (C=N), 196.7 (C=S). Found, %: C 46.82; H 4.07; N 14.99. $C_{11}H_{11}N_3S_3$. Calculated, %: C 46.95; H 3.94; N 14.93.

6-Phenyl-6,7-dihydro-5*H*-[1,2,4]dithiazolo[4,3-*a*]-[1,3,5]triazine-3-thione (9b) was prepared similarly using *i*-PrOH as solvent in the presence of Et_3N (1 eq.) and 10-fold excess of HCHO. Yield 9%, light-yellow powder. IR spectrum, ν, cm^{-1}: 3027, 2999, 2836 (C–H), 1598, 1537 (C=N, C=C), 1237, 1012 (C=S). ^{1}H NMR spectrum, δ, ppm: 4.89 br. s (2H, NCH_2N), 5.21 br. s (2H, NCH_2N), 6.80 t (1H, H^4_{Ar}, AB_2, ^3J = 7.2 Hz), 7.00 d (2H, $H^{2,6}_{Ar}$, ^3J = 8.1 Hz), 7.14–7.18 m (2H, $H^{3,5}_{Ar}$). ^{13}C NMR spectrum (DEPTQ), δ_C, ppm: 66.4 (CH_2N), 67.7 (CH_2N), 116.7*[1] (C^2, Ph), 119.8* (C^4, Ph), 129.1* ($C^{3,5}$, Ph), 147.0 (C^1, Ph), 180.3 (C=N), 208.3 (C=S).

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[1] (*) Signals in the antiphase.

Found, %: C 44.79; H 3.47; N 15.80. $C_{10}H_9N_3S_3$. Calculated, %: C 44.92; H 3.39; N 15.71.

Reaction of xanthane hydride 1 with HCHO and 2-nitroaniline. A mixture of 2-nitroaniline (0.58 g, 4.2 mmol), compound **1** (0.60 g, 4.0 mmol), excess of 21% aqueous solution of HCHO (5.65 mL, 4.0 mmol, *d* 1.062 g/mL), Et_3N (0.56 mL, 4.0 mmol), and 10 mL of EtOH was refluxed for 6 h. The precipitate was filtered off and recrystallized from acetone. 0.22 g of light-yellow powder was obtained. According to ^1H NMR spectroscopy data, it was a mixture of *N,N'*-bis(2-nitrophenyl)methanediamine **10** and [(2-nitrophenyl)-amino]methanol **11** in ratio ~ 3 : 4. IR spectrum, ν, cm^{-1}: 3405, 3392, 3372 (N–H, O–H), 1615 (C=C), 1505, 1501, 1341, 1329 (NO_2).

***N,N'*-Bis(2-nitrophenyl)methanediamine (10).** ^1H NMR spectrum, δ, ppm: 5.09 t (2H, $NHC\underline{H}_2NH$, ^3J = 5.6 Hz), 6.72–6.79 m (2H, 2 H^4_{Ar}, overlap with signals of compound **11**), 7.19 d (2H, 2 H^6_{Ar}, ^3J = 8.8 Hz), 7.46–7.57 m (2H, H^5_{Ar}, overlap with signals of compound **11**), 8.02 d (2H, 2 H^3_{Ar}, ^3J = 8.8 Hz), 8.69 t (2H, $N\underline{H}CH_2N\underline{H}$, ^3J = 5.6 Hz).

[(2-Nitrophenyl)amino]methanol (11). ^1H NMR spectrum, δ, ppm: 4.91 d (2H, $NHC\underline{H}_2OH$, ^3J = 6.5 Hz), 6.72–6.79 m (1H, H^4_{Ar}, overlap with signals of compound **10**), 7.46–7.57 m (2H, $H^{3,5}$Ar, overlap with signals of compound **10**), 8.02 d (1H, H^6_{Ar}, ^3J = 8.8 Hz), 8.75 t (1H, $N\underline{H}CH_2$, ^3J = 6.5 Hz). The signal of OH proton was not observed distinctly because of deuterium exchange.

4,6-Diamino-1,3,5-triazine-2(5*H*)-thione (thioammeline) (12). Xanthane hydride **1** (2.0 g, 0.0133 mol) and dicyanodiamide (1.12 g, 0.0133 mol) were dissolved in 5 mL of DMF at heating. The mixture was refluxed for 5 min. The formation of light-yellow precipitate was observed after ~2 min. The mixture was cooled down and diluted with 20 mL of EtOH. The precipitate was filtered off and dissolved in excess of 10% solution of KOH. The solution was filtered from sulfur and acidified with AcOH to pH 5–6. The precipitate was filtered off and dried. Yield 1.30 g (67%), mp 340°C (decomp.) (mp > 350°C [36]), colorless crystals, poorly soluble in EtOH, DMF, soluble in solutions of strong acids and bases. IR spectrum, ν, cm^{-1}: 3388, 3347, 3117 (N–H), 1683 (C=N), 1292, 1069 (C=S). ^1H NMR spectrum, δ, ppm: 6.81 br. s (2H, NH_2), 7.38 br. s (2H, NH_2), 11.20 br. s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 160.4 ($C^{4,6}$), 181.9 (C^2). Mass spectrum (ESI), *m/z*: 144 $[M + H]^+$, 217 $[M + DMF + H]^+$, 290 $[M + 2DMF + H]^+$. Found, %: C 25.15; H 3.59; N 48.90. $C_3H_5N_5S$. Calculated, %: C 25.17; H 3.52; N 48.92. *M* 143.17.

Corrosion study (potentiodynamic method). The 10×10×1 mm samples of steel 20 GOST 1050-2013 (%: C 0.17–0.24, Si 0.13–0.37, Mn 0.35–0.65, Cr < 0.25, Ni < 0.30, Fe the residue) were finished to roughness $R_a < 0.16$ μm, ungreased with ethanol, activated for 1 min in 15% HCl, and washed with distilled water. The experiments were carried out in the Holms borate buffer solution, pH 7.4 [39] using an IPC-Pro-L automated potentiostat and a standard three-electrode electrochemical cell. A Pt electrode was used as an auxiliary (polarizing) electrode; Ag,AgCl|KCl_{sat} electrode connected via a valve to avoid contamination of electrolyte with chloride ions was used as a reference electrode. Before the start of the measurements, the working electrode (tested sample) was kept at potential from –900 to –1000 mV for 15 min (hereafter the potentials are given with respect to the reference electrode) to remove the natural oxidation products from the surface. The anodic branch of the polarization curve was investigated at the potentials from –800 to 1600 mV with scanning rate 2 mV/s.

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CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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