

UDC 547.496.3+620.197.3

*D.A. Pisanenko, Yu.E. Klimko, O.V. Gaidai***SYNTHESIS AND ANTICORROSION PROPERTIES OF N-ARYL-N<sup>1</sup>-PYRIDYLTHIOUREAS AND THEIR BENZYLATED PRODUCTS****National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine**

N-Phenyl-, 1- and 2-naphthyl-N<sup>1</sup>-2- and 4-pyridylthioureas were synthesized via the reaction of phenyl-, 1- and 2-naphthylisothiocyanates with 2- and 4-aminopyridines, and the corresponding pyridine salts were prepared by benzylation of the latter. The anticorrosive properties of the synthesized compounds were studied by the gravimetric method in 3 M HCl at 80°C using the 08 kp steel samples. The introduction of a benzyl fragment into the structure of N-aryl-N<sup>1</sup>-pyridylthioureas led to the emergence of a new adsorption ammonium center, which increased the overall anti-corrosion efficiency of the obtained compounds. When using N-aryl-N<sup>1</sup>-pyridylthioureas, the corrosion inhibition coefficient had the values of 4.5 to 59.0, whereas it increased to 90.8-629.0 for their salts. To explain the different anti-corrosion activity of N-aryl-N<sup>1</sup>-pyridylthioureas and their pyridine salts, quantum-chemical calculations of the energy parameters  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$  were carried out and the dependences of the corrosion inhibition coefficients on  $E_{\text{HOMO}}$  and  $\Delta E$ ,  $e^{\Delta E}$  were obtained. A correlation was established between the inhibitory efficiency and energy parameters of the studied compounds.

**Keywords:** N-aryl-N<sup>1</sup>-pyridylthioureas, benzylated N-aryl-N<sup>1</sup>-pyridylthioureas, corrosion, corrosion inhibition coefficient, energy parameters.

**DOI:** 10.32434/0321-4095-2024-154-3-130-135

**Introduction**

Thiourea and its derivatives are quite strong inhibitors of acid corrosion [1], the protective effect of which is explained by the donor-acceptor interaction of the multiple bond and heteroatoms with the metal [2]. It is also known that the main factor affecting the effectiveness of most acid corrosion inhibitors is the presence of an ammonium center in their structure, due to which the inhibitor molecules are adsorbed on the metal surface [3]. The introduction of such a center into the structure of thiourea and its derivatives will enhance the overall protective effect of such compounds.

In addition, organic cations, which have a significant shielding effect, will also improve the protection of the metal [3]. In this regard, it is of interest to synthesize compounds of this structure that provide a total inhibitory effect and study their behavior in an acidic medium.

The aim of this work is, firstly, the one-step synthesis of N-aryl-N<sup>1</sup>-pyridylthioureas and their benzylation to obtain pyridinium salts, and secondly, the study of the anticorrosion properties of these compounds in an acidic medium.

**Experimental**

<sup>1</sup>H NMR spectra were recorded on BrukerAvance II 400 instrument (400.13 MHz) in DMSO-*d*<sub>6</sub> with TMS as internal reference, chemical shifts were measured in the  $\delta$  scale. IR spectra were recorded on Specord-75-JR spectrometer in KBr pellets. The purity of the obtained compounds was monitored by TLC and column chromatography on Merck silica gel 60F-254. Reagents of chemically pure grade were used for the experiments. For quantum chemical calculations, the Firefly software package [4] was used, partially based on the GAMESS (US) source code [5], according to the B3LYP method with the basic set 6-31G(d) [6,7], which allows finding the

© D.A. Pisanenko, Yu.E. Klimko, O.V. Gaidai, 2024



This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

*D.A. Pisanenko, Yu.E. Klimko, O.V. Gaidai*

conformation with the minimum energy and determining the energies of the HOMO and LUMO, as well as the charges of the adsorbed centers of the structure cations.

The starting *N*-aryl isothiocyanates (1)–(3) required for the synthesis of *N*-aryl-*N*<sup>1</sup>-pyridylthioureas (6)–(11) were obtained according to ref. [8,9]. *N*-Phenyl-*N*<sup>1</sup>-(2-pyridyl)thiourea (6) was prepared by the reaction of *N*-phenylisothiocyanate with 2-aminopyridine according to [10], *N*-aryl-*N*<sup>1</sup>-pyridylthiourea (7)–(10) was synthesized by the same method [11] as indicated on the scheme. The physicochemical constants of thioureas (6)–(10) and the data of their <sup>1</sup>HMR spectra corresponded to the literature data.

New thiourea (11) was synthesized in the same way as compounds (6)–(10). 2-Naphthylisothiocyanate (2.5 g, 13.0 mmol) and 4-aminopyridine (1.52 g, 16.0 mmol) are dissolved in 20 ml of pyridine. Leave overnight at room temperature under argon. The precipitate that forms is filtered off, washed with dry benzene and dried in air.

Yield 3.49 g (methanol–water), 92%; mp. 132°C. <sup>1</sup>H NMR (δ, ppm): 7.38 (2H, t, 8.0 Hz, 5,6-naphtyl), 7.48 (2H, t, 8.0 Hz, 7,8-naphtyl), 7.61 (1H, d, 8.5 Hz, 4-naphtyl), 7.78 (1H, d, 8.5 Hz, 3-naphtyl), 8.01 (1H, s, 1-naphtyl), 8.42 (2H, d, 6.0 Hz, 3-Py), 8.56 (2H, d, 6.0 Hz, 2-Py), 10.27 (2H, NH). IR, cm<sup>-1</sup>: 828 (CH, δ), 1125 (C=S, ν), 1365 (NH, δ), 1428 (4-Py, ν), 1525 (CN, ν), 1578 (CN, ν), 3080 (CH, ν).

*General procedures for benzylation of N-aryl-N<sup>1</sup>-pyridylthioureas*

7–9 mmol thiourea (6)–(11) and 7–14 mmol benzyl chloride were dissolved in 25–30 ml of dry benzene or CHCl<sub>3</sub>, boiled for 10–22 h. Then, the mixture was cooled and the solvent was evaporated in vacuum to a dry residue or precipitated from the reaction. The precipitate was filtered off, dried in a vacuum desiccator, and weighed. The yields of salts (12)–(17) were 44–98%. After further purification by recrystallization or by TLC or column chromatography, the melting point was determined, and elemental analysis and <sup>1</sup>H NMR spectrometry were performed. Physicochemical constants of salts (12)–(17) and data of <sup>1</sup>H NMR spectra are shown below and in Table 1.

*N<sup>1</sup>-(2-pyridyl-N-benzylpyridinium chloride)-N-(phenyl)thiourea (12)*

<sup>1</sup>H NMR (δ, ppm): 4.39 (2H, s, CH<sub>2</sub>), 7.12 (1H, t, 6.5 Hz, p-Ph), 7.18 (1H, t, 6.5 Hz, m-Ph), 7.22 (1H, 7.0 Hz, o-Ph), 7.26–7.46 (7H, m, Ph), 7.69 (1H, 8.0 Hz, 3-Py), 7.84 (1H, t, 8.0 Hz, 4-Py), 8.15 (1H, t, 8.0 Hz, 5-Py), 8.33 (1H, dd, 8.0 Hz,

4.0Hz, 6-Py), 10.88 (1H, s, NH), 13.82 (1H, s, NH). IR, cm<sup>-1</sup>: 1130 (C=S, ν), 1360 (NH, δ), 1528 (CN, ν), 1585 (CN, ν), 1620 (2-Py, ν), 1945 (CH, δ), 3020 (CH, ν), 3035 (CH, ν).

*N<sup>1</sup>-(2-pyridyl-N-benzylpyridinium chloride)-N-(1-naphthyl)thiourea (13)*

<sup>1</sup>H NMR (δ, ppm): 5.35 (2H, s, CH<sub>2</sub>), 6.80 (1H, t, 8.0 Hz, 6-naphtyl), 6.86 (1H, d, 8.0 Hz, 5-naphtyl), 7.11 (1H, d, 8.0 Hz, 8-naphtyl), 7.31–7.38 (5H, s, Ph), 7.45 (1H, d, 8.0 Hz, 3-Py), 7.57 (1H, d, 8.5 Hz, 4-naphtyl), 7.58 (1H, t, 8.0 Hz, 4-Py), 7.69 (1H, dd, 8.0 Hz, 4.0 Hz, 3-naphtyl), 7.89 (1H, δ, 8.5 Hz, 2-naphtyl), 8.08 (1H, t, 8.0 Hz, 7-naphtyl), 8.17 (1H, t, 8.0 Hz, 5-Py), 8.55 (1H, dd, 8.0 Hz, 4.0Hz, 6-Py), 10.09 (1H, s, NH), 11.45 (1H, s, NH). IR, cm<sup>-1</sup>: 840 (CH, δ), 1135 (C=S, ν), 1375 (NH, δ), 1532 (CN, ν), 1570 (CN, ν), 1615 (2-Py, ν), 3021 (CH, ν), 3035 (CH, ν).

*N<sup>1</sup>-(2-pyridyl-N-benzylpyridinium chloride)-N-(2-naphthyl)thiourea (14)*

<sup>1</sup>H NMR (δ, ppm): 5.65 (2H, s, CH<sub>2</sub>), 7.18 (1H, d, 8.5 Hz, 5-naphtyl), 7.25 (1H, t, 8.5 Hz, 6-naphtyl), 7.40 (1H, d, 8.0 Hz, 3-Py), 7.43 (1H, t, 8.5 Hz, 7-naphtyl), 7.46–7.49 (5H, s, Ph), 7.56 (1H, t, 8.0 Hz, 4-Py), 7.65 (1H, d, 8.5 Hz, 8-naphtyl), 7.95 (1H, s, 1-naphtyl), 8.15 (1H, t, 8.0 Hz, 5-Py), 8.27 (1H, d, 6.5 Hz, 4-naphtyl), 8.39 (1H, d, 6.5 Hz, 3-naphtyl), 8.51 (1H, dd, 8.0 Hz, 4.0Hz, 6-Py), 11.63 (1H, s, NH), 11.75 (1H, s, NH). IR, cm<sup>-1</sup>: 838 (CH, δ), 1142 (C=S, ν), 1365 (NH, δ), 1520 (CN, ν), 1565 (CN, ν), 3025 (CH, ν), 3080 (CH, ν).

*N<sup>1</sup>-(4-pyridyl-N-benzylpyridinium chloride)-N-(phenyl)thiourea (15)*

<sup>1</sup>H NMR (δ, ppm): 5.64 (2H, s, CH<sub>2</sub>), 7.24 (1H, t, 7.5 Hz, p-Ph), 7.39–7.45 (7H, m, Ph), 7.59 (2H, d, 9.0 Hz, o-Ph), 8.27 (2H, d, 8.0 Hz, 2-Py), 8.82 (2H, d, 8.0 Hz, 3-Py), 11.47 (1H, s, NH), 12.13 (1H, s, NH). IR, cm<sup>-1</sup>: 1126 (C=S, ν), 1357 (NH, δ), 1520 (CN, ν), 1420 (4-Py, ν), 1940 (CH, δ), 3015 (CH, ν), 3030 (CH, ν).

*N<sup>1</sup>-(4-pyridyl-N-benzylpyridinium chloride)-N-(1-naphthyl)thiourea (16)*

<sup>1</sup>H NMR (δ, ppm): 5.66 (2H, s, CH<sub>2</sub>), 6.76 (1H, t, 8.0 Hz, 6-naphtyl), 6.84 (1H, d, 8.0 Hz, 5-naphtyl), 7.14 (1H, d, 8.0 Hz, 8-naphtyl), 7.31–7.45 (5H, s, Ph), 7.57 (1H, d, 8.5Hz, 4-naphtyl), 7.67 (1H, dd, 8.0 Hz, 4.0Hz, 3-naphtyl), 7.91 (1H, d, 8.5 Hz, 2-naphtyl), 7.99 (1H, t, 8.0 Hz, 7-naphtyl), 8.27 (2H, d, 5.0 Hz, 3-Py), 8.86 (2H, d, 5.0 Hz, 2-Py), 12.58 (1H, s, NH), 13.16 (1H, s, NH). IR, cm<sup>-1</sup>: 860 (CH, δ), 1130 (C=S, ν), 1362 (NH, δ), 1415 (4-Py, ν), 1525 (CN, ν), 1582 (CN, ν), 3021 (CH, ν), 3070 (CH, ν).

*N*'-(4-pyridyl-*N*-benzylpyridinium chloride)-*N*-(2-naphthyl)thiourea (17)

<sup>1</sup>H NMR (δ, ppm): 5.87 (2H, s, CH<sub>2</sub>), 7.43–7.46 (6H, m, Ph, 7-naphtyl), 7.52 (1H, t, 8.0 Hz, 6-naphtyl), 8.21 (1H, d, 7.5 Hz, 4-naphtyl), 8.34 (1H, d, 7.5 Hz, 3-naphtyl), 8.86 (2H, d, 9.0 Hz, 3-Py), 9.24 (2H, d, 9.0 Hz, 2-Py), 11.75 (1H, s, NH), 12.36 (1H, s, NH). IR, cm<sup>-1</sup>: 810 (CH, δ), 1126 (C=S, ν), 1355 (NH, δ), 1410 (4-Py, ν), 1525 (CN, ν), 1575 (CN, ν), 3020 (CH, ν), 3068 (CH, ν).

#### Anticorrosion activity

Corrosion tests were carried out in 3 M HCl at 80°C by gravimetric method using the 08 kp steel samples of cylinder form (diameter of 11 mm and height of 20 mm) polished to the 5 class of accuracy. Before being placed in the medium corrosion, the steel samples were cleaned with acetone and dried in a silica gel desiccator for 5–6 hours. After completion of the experiment, the sample was washed with distilled water and dried at 150°C for 0.5 h. Then, they were weighed by analytical scales. 0.01 mol·L<sup>-1</sup> of the synthesized compounds were used for inhibition, the tests period being 0.25 h. Corrosion inhibition coefficient was calculated using the following formula:

$$\gamma = i/i'$$

where *i* and *i'* are the corrosion rates in the absence and in the presence of the inhibitor, respectively [3].

The reduced corrosion inhibitory coefficient [γ], taking into account the molar mass of organic inhibitors, was calculated by the following formula:

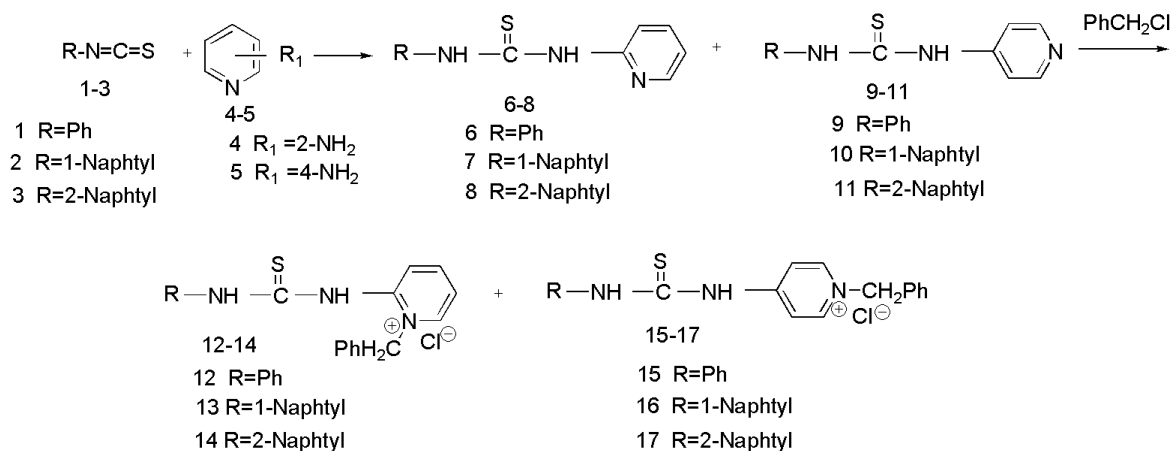
$$[\gamma] = \gamma/M,$$

where *M* is the molar mass of the inhibitor.

#### Results and discussion

*N*-Aryl-*N*'-pyridylthioureas (6)–(10) were prepared by a one-step synthesis with 63–89% yields. Undescribed *N*-(2-naphthyl)-*N*'-(4-pyridyl)thiourea (11) was synthesized by the same method, elemental analysis data corresponded to its empirical formula, and the <sup>1</sup>H NMR spectrum contained a broadened singlet of 2 protons of the NH groups at 10.27 ppm (Scheme, Table 1).

The pyridinium salts (12)–(17) were obtained by benzylation of thioureas (6)–(11), the elemental analysis data also corresponded to their empirical formulas, and their <sup>1</sup>H NMR spectra contained signals methylene protons of CH<sub>2</sub>– groups of benzyl radicals at 5.87–7.39 ppm, signals of 2 protons of NH groups at 10.09–12.56 and 11.45–13.82 ppm (Scheme, Table 1).



Scheme

Table 1

Physicochemical constants of synthesized salts (12)–(17)

Compound	mp, °C	Found, %		Formula	Calculated, %		<sup>1</sup> H NMR, s, (1H) NH	Yield, %
		Cl	N		Cl	N		
12	162	10.74	11.17	C <sub>19</sub> H <sub>18</sub> ClN <sub>3</sub> S	10.11	11.80	10.88; 13.82	62
13	195	8.83	10.30	C <sub>23</sub> H <sub>20</sub> ClN <sub>3</sub> S	8.87	10.34	10.09; 11.45	56
14	234	8.82	10.30	C <sub>23</sub> H <sub>20</sub> ClN <sub>3</sub> S	8.87	10.34	11.63; 11.75	60
15	200	10.09	11.77	C <sub>19</sub> H <sub>18</sub> ClN <sub>3</sub> S	10.11	11.80	11.47; 12.13	44
16	120	8.83	10.29	C <sub>23</sub> H <sub>20</sub> ClN <sub>3</sub> S	8.87	10.34	12.58; 13.16	65
17	90	8.82	10.33	C <sub>23</sub> H <sub>20</sub> ClN <sub>3</sub> S	8.87	10.34	11.75; 12.36	98

To evaluate the anticorrosion properties of the synthesized compounds, we studied their effect on the corrosion of steel 08 kp in 3 M HCl at 80°C for 0.25 h, using them in an amount of 0.01 mol. We determined the corrosion inhibition coefficient  $\gamma$  and recalculated it into the reduced corrosion inhibition coefficient  $[\gamma]$ , taking into account the molecular weight of the tested compounds.

As can be seen from Table 2, the anticorrosion properties of thioureas (6)–(11) and their pyridinium salts (12)–(17) differ sharply. The first exhibit a rather weak protective effect, the values of the coefficient  $\gamma$  being in the range from 4.4 to 59.1 when they are used. This can be explained by the fact that the ability of the molecules of these thioureas to be adsorbed on the metal surface and protect it from corrosion is limited only by the donor-acceptor interaction  $\pi$ -electrons of a multiple bond and p-electrons of heteroatoms with vacant metal orbitals [2], which is affected by the size and spatial arrangement of the phenyl, naphthyl, and pyridyl radicals.

The introduction of a benzyl radical into the structure of synthesized urea molecules to obtain salts (12)–(17) leads to the formation of a new, stronger adsorption ammonium center, which creates intramolecular synergy and the inhibitory effect is sharply enhanced (Table 2). In the series of benzylated thioureas (12)–(17), the salts (12) and (15) are the least active as inhibitors, since there is a phenyl radical in their structure. In the presence of naphthyl radicals in the structure, the anticorrosion properties naturally increase by almost 4 times and the coefficient  $\gamma$  increases to 421.7–629.1, which can be explained both by the stronger blocking effect of these radicals and by the

energy parameters of the cations of such salts adsorbed on the metal surface. It is known from the literature [12] that such parameters can be the energies of the frontier orbitals  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ .

We carried out quantum-chemical calculations of these parameters for salt cations (12)–(17), and the results, as well as the values of the coefficients  $\gamma$  and  $[\gamma]$  are shown in Table 3. These data confirm the dependence of inhibitory effects on energy characteristics [12–15].

Table 3 shows the dependence of the anticorrosion properties of the studied salts on the  $E_{\text{HOMO}}$  value of the following order (14) > (13) > (16) > (17) > (12) > (15), and the decreasing the values of  $\Delta E$  occur in the following series (15) > (12) > (17) > (16) > (13) > (14), which correlates with values  $\gamma$  and  $[\gamma]$ . According to data shown in Table 3, a linear dependence  $[\gamma]$  vs.  $\Delta E$  was constructed and an approximation was carried out ( $R=0.96$ ). For the dependence  $[\gamma]$  vs.  $e^{\Delta E}$ , the correlation coefficient has a more correct value, 0.99, than that given elsewhere [12,13] when studying the anticorrosion properties of other amines. When applying the IMCA principle to the processes of metal dissolution and corrosion inhibition, the investigated compounds (12)–(17) can be attributed to «hard» molecules due to the  $\Delta E$  values found for them and having the ability to create strong bonds with the metal surface.

### Conclusions

N-aryl-N<sup>1</sup>-pyridylthioureas were prepared by a one-step synthesis, and pyridine salts were synthesized by benzylation with 44–98% yields. The anticorrosive properties of the synthesized compounds were studied by corrosion tests of the 08kp steel in 3 M HCl at

Table 2  
Influence of thioureas (7)–(8), (10)–(11) and products of their benzylation (12)–(17) on the corrosion of steel 08 kp in 3 M HCl at 80°C for 0.25 h

Corrosion inhibition coefficient	Compound									
	7	8	10	11	12	13	14	15	16	17
$\gamma$	10.2	59.1	52.7	4.4	163.8	596.7	629.1	90.8	466.3	421.7
$[\gamma]$	0.04	0.21	0.19	0.02	0.46	1.47	1.55	0.26	1.15	1.04

Table 3  
Inhibitory effect and quantum-chemical parameters of cations of compounds (12)–(17)

Compound	$E_{\text{HOMO}}$ , eV	$E_{\text{LUMO}}$ , eV	$\Delta E$ , eV	$e^{\Delta E}$	$\gamma$	$[\gamma]$
12	–11.31	–2.12	9.19	9820.00	163.81	0.46
13	–8.23	–5.60	2.63	13.90	596.65	1.47
14	–8.06	–5.71	2.35	10.50	629.11	1.55
15	–11.21	–1.92	9.29	10860.00	90.77	0.26
16	–8.66	–5.34	3.32	27.72	466.33	1.15
17	–8.72	–5.35	3.37	29.14	421.72	1.04

80°C for 0.25 h. The introduction of the benzyl fragment into the structure of N-aryl-N<sup>1</sup>-pyridylthioureas leads to the emergence of a new adsorption ammonium center, which enhances the overall anticorrosive efficiency of the obtained compounds. The coefficient of corrosion inhibition  $\gamma$  when using N-aryl-N<sup>1</sup>-pyridylthioureas as inhibitors, having a value from 4.5 to 59.0, increases for their pyridinium salts to 90.8–629.0. For the latter, the reduced corrosion inhibition coefficient [ $\gamma$ ] correlates better than the coefficient  $\gamma$  with such energy characteristics of the cations of these salts as  $E_{\text{HOMO}}$  and  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ .

## REFERENCES

1. *Reshetnikov S.M.* Inhibitory kislотноi korrozii metallov. – Leningrad: Khimiya, 1986. – 144 p.
2. *Kuznetsov Yu.I., Kazansky L.P.* Physicochemical aspects of metal protection by azoles as corrosion inhibitors // *Russ. Chem. Rev.* – 2008. – Vol.77. – No. 3. – P.219-232.
3. *Antropov L.I., Makushin E.M., Panasenko V.F.* Inhibitory korrozii metallov. – Kiev: Tekhnika, 1981. – 183 p.
4. *Granovsky A.A.* Firefly version 8. – Available from: <http://classic.chem.msk.su/gran/firealy.index.html>.
5. *General atomic and molecular electronic structure system / Schmidt M.W., Baldrige K.K., Boatz J.A., Elbert S.T., Gordon M.S., Jensen J.H., et al.* // *J. Comput. Chem.* – 1993. – Vol.14. – P.1347-1363.
6. *Electronegativity: the density functional viewpoint / Parr R.G., Donnelly R.A., Levy M., Palke W.E.* // *J. Chem. Phys.* – 1978. – Vol.68. – P.3801-3807.
7. *Parr R.G., Pearson R.G.* Absolute hardness: companion parameter to absolute electronegativity // *J. Am. Chem. Soc.* – 1983. – Vol.105. – P.7512-7516.
8. *A new efficient synthesis of isothiocyanates from amines using di-tert-butyl dicarbonate / Munch H., Hansen J.S., Pittelkow M., Cristensen J.B., Boas U.* // *Tetrahedron Lett.* – 2008. – Vol.49. – P.3117-3119.
9. *Feng W., Zhang X.G.* Organophosphine-free cooper-catalyzed isothiocyanation of amines with sodium bromodifluoroacetate and sulfur // *Chem. Commun.* – 2019. – Vol.55. – No. 8. – P.1144-1147.
10. *Synthesis and in vitro urease activity of N,N<sup>1</sup>-disubstituted thioureas / Khan K.M., Naz F., Taha M., Khan A., Perveen S., Choudhary M.I., et al.* // *Eur. J. Med. Chem.* – 2014. – Vol.74. – P.314-323.
11. *NN'-Diarylthioureas and related compounds of potential biological interest / Buu-Hoi N.P., Xuong N.D., Nam N.H.* // *J. Chem. Soc.* – 1955. – P.1573-1581.
12. *Sastri V.S., Perumareddi J.R.* Molecular orbital theoretical studies of some organic corrosion inhibitors // *Corrosion.* – 1997. – Vol.53. – No. 8. – P.617-622.
13. *DFT-study of new bipyrazole derivatives and their potential activity as corrosion inhibitors / Wang H., Wang X., Wang H., Wang L., Lui A.* // *J. Mol. Model.* – 2007. – Vol.13. – P.147-153.
14. *Lukovits J., Shaban A., Kalman E.* Corrosion inhibitors: quantitative structure – activity relationships // *Russ. J. Electrochem.* – 2003. – Vol.39. – P.177-181.
15. *Dependence of anti-corrosion properties on the energy characteristics of benzylated N-arylnicotinamides / Pisanenko D.A., Klimko Yu.E., Gaidai A.V., Dubskaya S.V.* // *Pharm. Chem. J.* – 2020. – Vol.7. – No. 2. – P.64-67.

Received 12.05.2023

## СИНТЕЗ ТА АНТИКОРРОЗІЙНІ ВЛАСТИВОСТІ N-АРИЛ-N<sup>1</sup>-ПІРИДИЛТІОМОЧОВИН І ПРОДУКТІВ ЇХ БЕНЗИЛЮВАННЯ

*Д.А. Писаненко, Ю.Є. Клишко, А.В. Гайдай*

Реакцією феніл-, 1- та 2-нафтилізотіоціанатів з 2- та 4-амінопіридинами синтезовано N-феніл-, 1- та 2-нафтил-N<sup>1</sup>-2- та 4-піридилтіомочевини, бензилюванням останніх одержані відповідні піридинові солі. Антикорозійні властивості синтезованих сполук вивчені гравіметричним методом у середовищі 3 М НСІ при 80°C з використанням зразків сталі 08 кп. Введення в структуру N-арил-N<sup>1</sup>-піридилтіомочевин бензильного фрагмента приводить до появи нового адсорбційного амонійного центру, що посилює загальну антикорозійну ефективність одержаних сполук. Коефіцієнт гальмування корозії при використанні N-арил-N<sup>1</sup>-піридилтіомочевин, що має величину від 4,5 до 59,0, збільшується для їх солей до 90,8–629,0. Для пояснення різної антикорозійної активності N-арил-N<sup>1</sup>-піридилтіомочевин та їх піридинових солей були проведені квантово-хімічні розрахунки енергетичних параметрів  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  та  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$  і надані залежності коефіцієнтів гальмування корозії від  $E_{\text{HOMO}}$ ,  $\Delta E$  і  $e^{\Delta E}$ . Встановлено кореляцію між інгібуючою ефективністю та енергетичними параметрами вивчених сполук.

**Ключові слова:** N-арил-N<sup>1</sup>-піридилтіомочевини, бензилювані N-арил-N<sup>1</sup>-піридилтіомочевини, корозія, коефіцієнт гальмування корозії, енергетичні параметри.

**SYNTHESIS AND ANTICORROSION PROPERTIES OF N-ARYL-N<sup>1</sup>-PYRIDYLTHIOUREAS AND THEIR BENZYLATED PRODUCTS***D.A. Pisanenko*\*, *Yu.E. Klimko*, *O.V. Gaidai*

National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine

\* e-mail: dpisanenko@ukr.net

N-Phenyl-, 1- and 2-naphthyl-N<sup>1</sup>-2- and 4-pyridylthioureas were synthesized via the reaction of phenyl-, 1- and 2-naphthylisothiocyanates with 2- and 4-aminopyridines, and the corresponding pyridine salts were prepared by benzylation of the latter. The anticorrosive properties of the synthesized compounds were studied by the gravimetric method in 3 M HCl at 80°C using the 08 kp steel samples. The introduction of a benzyl fragment into the structure of N-aryl-N<sup>1</sup>-pyridylthioureas led to the emergence of a new adsorption ammonium center, which increased the overall anti-corrosion efficiency of the obtained compounds. When using N-aryl-N<sup>1</sup>-pyridylthioureas, the corrosion inhibition coefficient had the values of 4.5 to 59.0, whereas it increased to 90.8-629.0 for their salts. To explain the different anti-corrosion activity of N-aryl-N<sup>1</sup>-pyridylthioureas and their pyridine salts, quantum-chemical calculations of the energy parameters  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$  and  $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$  were carried out and the dependences of the corrosion inhibition coefficients on  $E_{\text{HOMO}}$  and  $\Delta E$ ,  $e^{\Delta E}$  were obtained. A correlation was established between the inhibitory efficiency and energy parameters of the studied compounds.

**Keywords:** N-aryl-N<sup>1</sup>-pyridylthioureas; benzylated N-aryl-N<sup>1</sup>-pyridylthioureas; corrosion; corrosion inhibition coefficient; energy parameters.

**REFERENCES**

1. Reshetnikov SM. *Ingibitory kislotnoi korrozii metallov* [Inhibitors of acid corrosion of metals]. Leningrad: Khimiya; 1986. 144 p. (in Russian).
2. Kuznetsov YuI, Kazansky LP. Physicochemical aspects of metal protection by azoles as corrosion inhibitors. *Russ Chem Rev.* 2008; 77(3): 219-232. doi: 10.1070/RC2008v077n03ABEH003753.
3. Antropov LI, Makushin EM, Panasenko VF. *Ingibitory korrozii metallov* [Inhibitors of corrosion of metals]. Kiev: Tekhnika; 1981. 183 p. (in Russian).
4. Granovsky AA. *Firefly version 8* [Internet]. Available from: <http://classic.chem.msu.su/gran/firefly/index.html>.
5. Schmidt MW, Baldrige KK, Boatz JA, Elbert ST, Gordon MS, Jensen JH, et al. General atomic and molecular electronic structure system. *J Comput Chem.* 1993; 14: 1347-1363. doi: 10.1002/jcc.540141112.
6. Parr RG, Donnelly RA, Levy M, Palke WE. Electronegativity: the density functional viewpoint. *J Chem Phys.* 1978; 68: 3801-3807. doi: 10.1063/1.436185.
7. Parr RG, Pearson RG. Absolute hardness: companion parameter to absolute electronegativity. *J Am Chem Soc.* 1983; 105: 7512-7516. doi: 10.1021/ja00364a005.
8. Munch H, Hansen JS, Pittelkow M, Cristensen JB, Boas U. A new efficient synthesis of isothiocyanates from amines using di-tert-butyl dicarbonate. *Tetrahedron Lett.* 2008; 49: 3117-3119. doi: 10.1016/j.tetlet.2008.03.045.
9. Feng W, Zhang XG. Organophosphine-free cooper-catalyzed isothiocyanation of amines with sodium bromodifluoroacetate and sulfur. *Chem Commun.* 2019; 55: 1144-1147. doi: 10.1039/C8CC09190K.
10. Khan KM, Naz F, Taha M, Khan A, Perveen S, Choudhary MI, et al. Synthesis and in vitro urease activity of N,N<sup>1</sup>-disubstituted thioureas. *Eur J Med Chem.* 2014; 74: 314-323. doi: 10.1016/j.ejmech.2014.01.001.
11. Buu-Hoi NP, Xuong ND, Nam NH. NN'-Diarylthioureas and related compounds of potential biological interest. *J Chem Soc.* 1955; 1573-1581. doi: 10.1039/JR9550001573.
12. Sastri VS, Perumareddi JR. Molecular orbital theoretical studies of some organic corrosion inhibitors. *Corrosion.* 1997; 53(8): 617-622. doi: 10.5006/1.3290294.
13. Wang H, Wang X, Wang H, Wang L, Lui A. DFT-study of new bipyrazole derivatives and their potential activity as corrosion inhibitors. *J Mol Model.* 2007; 13: 147-153. doi: 10.1007/s00894-006-0135-x.
14. Lukovits I, Shaban A, Kalman E. Corrosion inhibitors: quantitative structure-activity relationships. *Russ J Electrochem.* 2003; 39: 177-181. doi: 10.1023/A:1022313126231.
15. Pisanenko DA, Klimko YuI, Gaidai AV, Dubskaya SV. Dependence of anti-corrosion properties on the energy characteristics of benzylated N-arylnicotinamides. *Pharm Chem J.* 2020; 7(2): 64-67.