ISSN 2070-2051, Protection of Metals and Physical Chemistry of Surfaces, 2010, Vol. 46, No. 1, pp. 71–74. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © V.N. Chelyabieva, O.I. Sizaya, S.V. Gatsenko, O.L. Gumenyuk, A.N. Esipenko, V.N. Britsun, 2009, published in Fizikokhimiya Poverkhnosti i Zashchita Materialov, 2009, Vol. 45, No. 6, pp. 699–702.

MOLECULAR AND SUPRAMOLECULAR SPECIES AT INTERFACE

Effect of the Nature and Position of Substituents on the Protective Properties of [1,3]Thiazino[3,2-a]benzimidazol-4-ones

**V. N. Chelyabieva[a], O. I. Sizaya[a], S. V. Gatsenko[a], O. L. Gumenyuk[a],
A. N. Esipenko[b], and V. N. Britsun[b]**
[a]*Chernigov State Technological University, ul. Shevchenko 95, Chernigov, 14027 Ukraine*
[b]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya ul. 5, Kiev, 02660 Ukraine*
e-mail: syza@rambler.ru

Received December 26, 2007

Abstract—Effect of the nature and position of substituents in [1,3]thiazino[3,2-*a*]benzimidazol-4-ones on their efficiency as corrosion inhibitors for steel 20 (HCl, pH 0) was studied.

PACS number:
DOI: 10.1134/S2070205110010107

INTRODUCTION

Many authors studied the effect of the structure of heterocyclic compounds on the efficiency of corrosion protection of metals [1–5]. These studies provide an opportunity for the purposeful synthesis of heterocyclic compounds with high efficiency of corrosion protection in a determined medium.

We showed recently [6] that [1,3]thiazino[3,2-a]benzimidazol-4-ones (TBIs) behave as multifunctional compounds, including acid corrosion inhibitors for steel, efficient additives for epoxy powder coatings that increase anticorrosive properties, and accelerants for the curing of epoxy oligomers. It was revealed that TBIs with electron-donating substituent OCH_3 in the molecule show high anticorrosive properties, whereas the replacement of the substituent with NO_2 group (exhibiting the electron-withdrawing effect) inhibits the adsorption of TBI on steel surface and prevents the formation of tightly adhered protective adsorptive films on metal surface. These results raise following questions of whether the introduction of additional OCH_3 groups in molecule enhances the anticorrosion effect and how the nature of the electron-withdrawing substituent affects the adsorption of inhibitor on the steel surface.

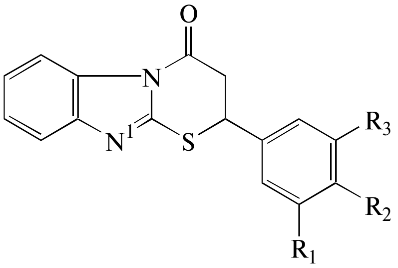
The present work deals with the target-directed synthesis of [1,3]thiazino[3,2-a]benzimidazol-4-ones and the study of the effect of the nature and position of substituents in the molecule on protection efficiency for steel 20 in a hydrochloric acid solution.

EXPERIMENTAL

The synthesis of TBIs (Table 1) was carried out according to the previously described procedure [6, 7]. The structure of obtained compounds was confirmed by ^{1}H NMR spectroscopy (using a Varian VXR-300 spectrometer) and elemental analysis data as follows:

TBI-2, yield 67%, mp 170–173°C. Anal. calcd. for $C_{18}H_{16}N_2O_3S$ (%): C, 63.53; H, 4.70; N, 8.23. Found

Table 1. Chemical structure of TBIs*



Additive	-R_1	-R_2	-R_3	Mr
TBI-1**	H	OCH_3	H	310
TBI-2	OCH_3	OCH_3	H	340
TBI-3	OCH_3	OCH_3	OCH_3	370
TBI-4**	H	NO_3	H	325
TBI-5	H	Cl	H	314
TBI-6	H	F	H	298
TBI-7	NO_2	H	H	325

Notes: * An erratum appeared in the Protection of Metals, 2007, vol. 43, no. 3, pp. 280–284. In the general formula of TBI, index 1 should show the same nitrogen atom as in the present paper. This atom is discussed in the paper.)
** Data for TBI-1 and TBI-4 are taken from previous paper [6].)

Table 2. Electrochemical parameters for corrosion of steel 20 in 1M HCl (C_{TBI} = 1 mmol/L)

Additive	Corrosion current, A/m^2			Corrosion potential, V			$\Delta\Psi_1$, V	Tafel equation constants			
	I_{corr}	I_c	I_a	$-E_{corr}$	$-E_c$	$-E_a$		a_c	a_a	b_c	b_a
Without TBI	7.94	89.13	199.53	0.290	0.390	0.240	–	0.72	0.48	0.14	0.08
TBI-1	0.52	5.01	19.95	0.310	0.550	0.150	0.124	0.89	0.56	0.13	0.08
TBI-2	1.51	25.12	15.85	0.260	0.470	0.150	0.219	0.08	0.56	0.14	0.08
TBI-3	2.00	31.62	25.12	0.260	0.450	0.160	0.219	0.79	0.55	0.14	0.08
TBI-4	3.80	39.81	63.10	0.295	0.440	0.200	+0.058	0.80	0.55	0.14	0.08
TBI-5	2.51	39.18	25.12	0.260	0.430	0.160	0.146	0.81	0.55	0.14	0.08
TBI-6	1.54	22.39	25.12	0.270	0.450	0.160	0.146	0.81	0.55	0.14	0.08
TBI-7	3.16	63.10	28.15	0.260	0.410	0.170	0.219	0.74	0.54	0.14	0.08

Table 3. Inhibiting effect of TBIs in 1M HCl (C_{TBI} = 1 mmol/L)

Protection degree and drag factors	TBI-1	TBI-2	TBI-3	TBI-4	TBI-5	TBI-6	TBI-7
Z_{corr}, %	93.47	80.98	74.81	52.15	68.39	80.60	60.20
γ_{corr}	15.3	2.26	3.97	2.09	3.16	5.16	2.51
γ_c	17.7	3.55	2.82	2.24	2.24	3.98	1.41
γ_a	10.00	12.59	7.94	3.16	7.94	7.94	7.08

(%): C, 63.54; H, 4.58; N, 8.40. ^{1}H NMR (δ, ppm): 3.24 (m, 1H, H-3), 3.73 (d, 6H, 2CH_3O), 3.85 (m, 1H, H-3), 5.31 (m, 1H, H-2), 6.99–7.36 (m, 5H, Ar), 8.17 (d, 1H, Ar), 8.18 (d, 1H, Ar).

TBI-5, yield 73%, mp 148–151°C. Anal. calcd. for $C_{16}H_{11}ClN_2OS$ (%): C, 61.05; H, 3.52; N, 8.90. Found (%): C, 61.33; H, 3.54; N, 8.82. ^{1}H NMR (δ, ppm): 3.45 (m, 1H, H-3), 3.84 (m, 1H, H-3), 5.42 (m, 1H, H-2), 7.37 (m, 2H, Ar), 7.42–7.55 (m, 5H, Ar), 8.17 (d, 1H, Ar).

TBI-6, yield 71%, mp 135–138°C. Anal. calcd. for $C_{16}H_{11}FN_2OS$ (%): C, 64.44; H, 3.72; N, 9.40. Found (%): C, 64.31; H, 3.60; N, 9.53. ^{1}H NMR (δ, ppm): 3.43 (m, 1H, H-3), 3.80 (m, 1H, H-3), 5.41 (m, 1H, H-2), 7.26–7.59 (m, 7H, Ar), 8.16 (d, 1H, Ar).

TBI-7, yield 82%, mp 192–195°C. Anal. calcd. for $C_{16}H_{11}N_3O_3S$ (%): C, 59.08; H, 3.41; N, 12.92. Found (%): C, 59.24; H, 3.17; N, 13.12. ^{1}H NMR (δ, ppm): 3.55 (m, 1H, H-3), 3.93 (m, 1H, H-3), 5.59 (m, 1H, H-2), 7.39–8.40 (m, 8H, Ar).

The data of ^{1}H NMR spectroscopy and elemental analysis for TBI-1, TBI-3, and TBI-4 are reported in [7]. The protection efficiency of TBIs (1 mmol/L) was estimated by electrochemical method (using P-5827M potentiostat). Corrosion medium was a HCl solution. Polarization curves (20 mV/min) were measured from the stationary potential using a glass three-electrode electrochemical cell with a separated cathode and anode space using an end electrode made of steel 20 inserted in a PTFE housing [8]. Silver chloride and platinum electrodes were used as reference and auxiliary electrodes, respectively. The working electrode potential was recalculated to the standard hydrogen scale.

Polarization curves were used to calculate the potential (E_{corr}) and current (I_{corr}) of electrochemical corrosion, cathode (E_c at $\log I_c = 1.6$, I_c at $E_c = -0.44$ V), and anode (E_a at $\log I_a = 1.6$, I_a at $E_a = -0.18$ V) partial processes, Tafel equation constants (a_c, a_a, b_c, b_a), drag factors γ_{corr}, γ_c, γ_a ($\gamma = I/I'$, where I and I' are corrosion current without inhibitor and in the presence of inhibitor, respectively), adsorption potential shift ($\Delta\psi_1$), and the degree of protection $Z_{corr} = (1 - 1/\gamma_{corr}) \times 100\%$.

Efficient charges on atoms for TBI derivatives were calculated using software at the Frank J. Seiler Research Lab, US Air Force Academy (Colorado Springs, United States) according to the PM3 Hamiltonian method. PM3 is considered to be the most accurate method for calculating the electron and kinetic characteristics of molecular and thermodynamic functions, optimized configuration, etc. Unlike other methods, PM3 is used for molecules that contain not only elements of I and II periods, but also the majority of elements of main subgroups of the periodic system and certain transition metals.

The statistical treatment of the results of electrochemical measurements was carried out to a probability level of 0.95 and a number of measurements $n = 3$ [9].

RESULTS AND DISCUSSION

Obtained experimental data are given in Tables 2–5 and in the figure. The introduction of TBI in corrosive

Table 4. Hammett constants for -R_1,-R_2,and -R_3

Substituent	p-CH_3O-	m-CH_3O-	p-NO_2-	m-NO_2-	p-Cl-	p-F-
Hammett constant, σ	–0.268	0.115	0.780	0.710	0.227	0.062

Table 5. Effective charges of heteroatoms for TBIs (PM3 method)

Active centers of molecule	TBI-1	TBI-2	TBI-3	TBI-4	TBI-5	TBI-6	TBI-7
N_1	–0.003754	–0.002164	–0.004181	–0.005798	–0.000316	–0.000175	0.005116
N	0.315649	0.315526	0.313481	0.319218	0.317437	0.316760	0.315883
O	–0.297350	–0.299469	–0.301095	–0.291851	–0.297080	–0.296023	–0.293681
S	0.083633	0.085813	0.097696	0.099529	0.099263	0.091138	0.091940
Ph*	–0.418727	–0.282819	–0.141817	–0.638736	–0.514314	–0.381940	–0.631917

* Ph is a benzene ring of phenyl group.

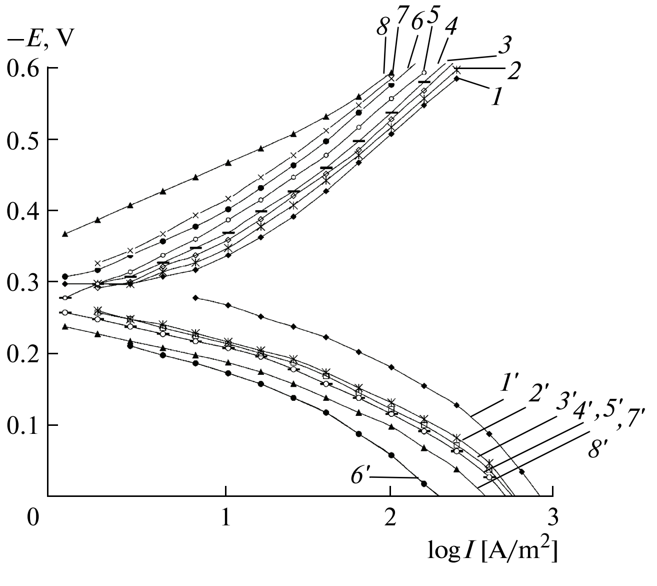
medium slightly changes the potential of free corrosion of steel 20 as follows: it drops by 20 mV for TBI-1 and increases by 20–30 mV for other additives (Table 2), which indicates the preferable inhibition of cathode or anode partial process, respectively, which agree with drag factors γ_c and γ_a (Table 3).

The comparative results of the inhibiting effect of TBI-1, TBI-2, and TBI-3 show that the insertion of additional OCH_3 groups (TBI-2 and TBI-3) at the meta position markedly decreases rather than increases protective properties; Z_{corr} is 93.47%, 80.98%, and 74.81% for TBI-1, TBI-2, and TBI-3, respectively. The introduction of the substituent at the position of R_1 for TBI-2 leads to the electron depletion of the N^1 nitrogen and benzene ring of the phenyl fragment in comparison with TBI-1. The introduction of the R_3 substituent leads to a slight increase in the electron density on N^1 nitrogen for TBI-3, but the electron density of Ph decreases by a factor of three (Table 5), which affects inhibition properties. The results agree well with the values of Hammett constants as follows: OCH_3 substituent shows electron-donating properties at the para position (R_2) but electron-withdrawing effect at the meta position (R_1, R_3) (Table 4). Thus, the introduction of additional OCH_3 groups in the meta position of the molecule decreases the anticorrosion properties.

To answer the question of the relationship between nature of substituents and the protective effect of TBI, we also prepared compounds TBI-5, TBI-6, and TBI-7 (Table 1). The relationship between Hammett σ-constants and protection efficiency is also observed in the series TBI-4, TBI-5, TBI-6, and TBI-1 (Tables 3, 4 and figure). Thus, the Hammett σ-constants of R_2 are +0.780, +0.227, +0.062, and –0.268, respectively, i.e., the electron-withdrawing effect decreases and drag factors for electrochemical corrosion increase to 2.09, 3.16, 5.16, and 15.3, respectively.

The adsorption centers of TBI are N^1, O, S atoms and benzene π electrons [6, 10]. The electron-donating substituent at the para position of phenyl fragment enhances the electron density at the N^1 nitrogen atom and has no significant effect on the efficient charges of heteroatoms of the thiazolone ring (Table 5), which facilitates specific type-2 adsorption on the steel surface and increases the anticorrosion effect of TBI.

The introduction of NO_2 substituent at the meta position of the phenyl fragment (TBI-7) instead of the para position (TBI-4) leads to a certain growth in the protection by 52.15% for TBI-4 and 60.20% for TBI-7. The electron density on the active centers of the molecules changes insignificantly, but electron-withdrawing properties are reduced when NO_2 substituent is located at the



Cathode (1–8) and anode (1'–8') polarization curves for steel 20 in 1M HCl in the presence of TBI: 1 and 1', no additive; 2 and 2', TBI-4; 3 and 3', TBI-7; 4 and 4', TBI-5; 5 and 5', TBI-3; 6 and 6', TBI-2; 7 and 7', TBI-6; 8 and 8', TBI-1.

meta position, which explains the growth in the degree of protection for TBI-7.

Thus, the analysis of the anticorrosion efficiency of TBI compounds confirms and supplements our previous conclusions [6]; the electron-donating and electron-withdrawing effect of substituent and its position in TBI molecule affect the efficient charges of main adsorption centers (the N^1 nitrogen atom and the benzene ring of phenyl fragment); the capacity for specific adsorption; and, therefore, anticorrosion properties.

CONCLUSIONS

(i) [1,3]Thiazino[3,2-*a*]benzimidazol-4-ones are inhibitors of acid corrosion of steel whose efficiency increases with electron-donating properties of substituents and decreases when electron-withdrawing effect rises. The anticorrosion effect increases upon the direct conjugation of electron-donating substituent with the main adsorption centers of the molecule.

(ii) The dependence of the anticorrosion effect of TBI on their structure allows the purposeful development of heterocyclic compounds as efficient inhibitors of acid corrosion.

REFERENCES

1. Grigor'ev, V.P. and Ekilik, V.V., *Khimicheskaya struktura i zashchitnoe deistvie ingibitorov korrozii* (Chemical Structure and Protective Effect of Corrosion Inhibitors), Rostov-on-Don: Izd. Rostov State Univ., 1978.
2. Ledovskikh, V.M., *Zashch. Met.*, 1983, vol. 19, no. 2, p. 290.
3. Makovei, G.L., Keris', L.D., and Kurmakova, I.N., *Zashch. Met.*, 1983, vol. 19, no. 3, p. 465.
4. Sizaya, O.I., Kosukhina, L.D., Chumakov, V.A., et al., *Zh. Prikl. Khim.*, 1996, vol. 69, no. 9, p. 1501.
5. Chernyad'ev, I.N., Shein, A.B., and Nedugov, A.N., *Zashch. Met.*, 2007, vol. 43, no. 3, p. 285.
6. Chelyabieva, V.N., Sizaya, O.I., Gatsenko, S.V., et al., *Zashch. Met.*, 2007, vol. 43, no. 3, p. 280.
7. Britsun, V.N. and Lozinskii, M.O., *Khim. Geterotsikl. Soedin.*, 2003, vol. 7, p. 1103.
8. Freiman L.I., Makarov V.A., and Bryksin I.E. *Potentsiostaticheskie metody v korrozionnykh issledovaniyakh v elektrokhimicheskoi zashchite* (Potentiostatic Methods in the Corrosion Studies of Electrochemical Protection), Leningrad: Khimiya, 1972.
9. Gordon, A. and Ford, R., *The Chemist's Companion*, New York: Wiley, 1972.
10. Reshetnikov, S.M., *Ingibitory kislotnoi korrozii metallov* (Inhibitors of Acid Corrosion of Metals), Leningrad: Khimiya, 1986.