

Structure, Anticorrosion and Antibacterial Evaluation of 1-(Morpholinomethyl)indoline-2,3-dione

GUO-XIN SUN^{1,*} and YAN-QING MIAO²

¹Sports Physiology Biochemistry of Laboratory of Physical Education Department, Southwest Jiaotong University, Chengdu 611756, P.R. China

²Department of Pharmacology, Xi'an Medical University, Xi'an 710068, P.R. China

*Corresponding author: Tel./Fax: +86 29 88382693; E-mail: miaoyanqing2006@163.com

Received: 22 April 2014;

Accepted: 8 July 2014;

Published online: 6 November 2014;

AJC-16238

In this paper, 3-(4-hydroxyphenylimino)indolin-2-one, was synthesized and analyzed by NMR, MS and X-ray single crystal analysis. The inhibition and the mechanism of the compound on the corrosion of high protective Q235A steel in HCl solution were screened and discussed. The results indicated that it can inhibit the corrosion with moderate inhibition efficiency in different conditions and the inhibition mechanism of the corrosion inhibiting may be mainly contributed to the adsorption. It was screened for antibacterial activity against oilfield water-borne bacteria and it showed good to moderate activity against sulfate reducing bacteria.

Keywords: Indole-2,3-dione, Mannich base, Corrosion inhibition, Adsorption, Microbiologically influenced corrosion.

INTRODUCTION

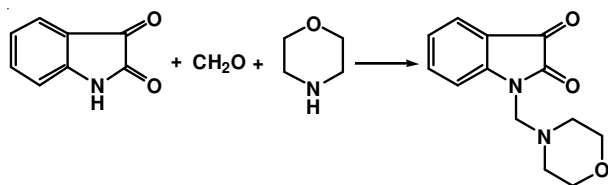
Indole-2,3-dione is a compound found in *Strobilanthes cusia* (Nees) Kuntze and many other plants such as genus *Isatis*, *Calanthe discolor* Lindl., *Couroupita guianensis* Aubl. and in mammalian tissue¹. It displays versatile bioactivity and it is used to synthesize a large variety of heterocyclic compounds in preparing drugs²⁻⁴. Indole-2,3-dione Mannich bases are reported to have antibacterial activities^{5,6}.

Compounds, containing functional electronegative groups and p and/or π -electron in triple or conjugated double bonds, are found to be efficient as inhibitors against metal corrosion^{7,8}. It has been commonly recognized that an organic inhibitor usually promotes formation of a chelate on a metal surface, by transferring p and/or π -electrons from the organic compounds to the metal and forming a coordinate covalent bond during the chemical adsorption⁹⁻¹¹. Organic compounds, containing heteroatoms, such as sulfur, phosphorus, nitrogen and oxygen, together with aromatic rings in their structure are the major adsorption centers and the Schiff bases, a condensation product of an amine and a ketone/aldehyde, are such typical molecules¹²⁻¹⁴. Some polydentate Schiff base compounds have been reported as effective corrosion inhibitors for various metals in acid media^{13,15-17}. Several indole-2,3-dione derivatives have been reported as inhibitors in HCl solution¹⁸⁻²⁰. The aim of this work is to screen the inhibitory action of 1-(morpholinomethyl)indoline-2,3-dione for the corrosion of mild steel both in high concentrated HCl solution and microbiologically influenced corrosion.

EXPERIMENTAL

Synthesis of 1-(morpholinomethyl)indoline-2,3-dione: 1-(Morpholinomethyl)indoline-2,3-dione was synthesized according to published methods (**Scheme-I**). Indole-2,3-dione (1 mmol), formaldehyde (1.1 mmol) and morpholin (1.1 mmol) were dissolved in methanol (30 mL). The mixture was refluxed until the disappearance of indole-2,3-dione, as evidenced by thin-layer chromatography. The solvent was removed *in vacuo* and the residue was separated by column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1), giving the title compound. ¹H NMR (D₆-DMSO, 400 MHz): 7.61 (2H, m), 7.15 (1H, t, $J = 7.2$ Hz), 7.09 (1H, d, $J = 8.0$ Hz), 4.45 (2H, s), 3.70 (4H, t, $J = 4.8$ Hz), 2.63 (4H, t, $J = 4.8$ Hz); MS (EI) m/z : 246 (M^+). 20 mg of the title compound was dissolved in 50 mL methanol and the solution was kept at room temperature for 7 d, natural evaporation gave orange single crystals of the title compound suitable for X-ray analysis.

X-ray data collection and structure refinement: Intensity data for colourless crystals of compound **4** was collected at 150 K on a Bruker SMART 1000 CCD fitted with MoK α radiation. The data sets were corrected for absorption based on multiple scans and reduced using standard methods. The structures was solved by direct-methods¹³ and refined by a full-matrix leastsquares procedure on F^2 with anisotropic displacement parameters for non-hydrogen atoms, carbon- and nitrogen bound hydrogen atoms in their calculated positions and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were positioned



Scheme-1: Synthesis of 1-(morpholinomethyl)indoline-2,3-dione

geometrically and allowed to ride on their parent atoms, with $d(\text{N-H}) = 0.86 \text{ \AA}$ and $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{N})$, $d(\text{C-H}) = 0.93$ or $0.96 (\text{CH}_3) \text{ \AA}$ and $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{C})$ or $1.5 \text{ Ueq}(\text{C})$. Crystal data and refinement details were given in Table-1.

Gravimetric measurements: The corrosion tests were performed on Q235A with a composition (in wt. %) C: 0.22, P: 0.045, Si: 0.35, S: 0.05, Mn: 1.40 and Fe balance. The electrolyte solution was 3M HCl, prepared from analytical grade 38 % HCl and distilled water. The concentration range of 3-(4-hydroxyphenylimino)indolin-2-one was employed as 0.05 and 0.10 g/L. All tests have been performed in deaerated solutions and at $60 \pm 0.5 \text{ }^\circ\text{C}$. The gravimetric tests were carried out according to the People's Republic of China Standard of Petroleum and Natural Gas Industry (Evaluation method for behaviour of corrosion inhibitor for produced water of oilfield, SY/T5273-2000) with a few modifications. Each test was done with three specimens at the same time to give reproducible results.

Microbiological monitoring: Viable counts of SRB, TGB and FB were determined with the "most probable number" method, People's Republic of China Standard of Petroleum and Natural Gas Industry, the national method of the bactericidal agent's performance, SY/T 5890-1993). The produced water containing the three kinds of bacteria was gathered from Zichang Oilfield Factory, Yanchang Oilfield.

RESULTS AND DISCUSSION

Structure: The X-ray structural analysis confirmed the assignment of its structure from spectroscopic data. Geometric parameters of 1-(morpholinomethyl)indoline-2,3-dione are in the usual ranges. The atomic coordinates are displayed in Table-2 and the molecular structure is shown in Fig. 1. The space-group is $P 1 2_1/c 1$ with a monoclinic crystal system. The indol-2-one ring system is substantially planar and the morpholin ring displays a typical chair conformation, with the 2,3-dioxindolin-1-yl)methyl group in equatorial position. In the crystal structure, molecules are kinked into a three-dimensional network by $\text{C-H}\cdots\text{O}$ hydrogen bonds as shown in Fig. 2 and the hydrogen bonds parameters are included in Table-3.

Inhibitor properties and mechanism: Corrosion can be defined as the degradation of a material due to a reaction with its environment. Degradation implies deterioration of physical properties of the material. This can be a weakening of the

TABLE-1
EXPERIMENTAL DATA OF 1-(MORPHOLINOMETHYL)INDOLINE-2,3-DIONE

Crystal parameter	Data	Crystal parameter	Data
a (Å)	11.608(2)	Index ranges	$-4 \leq h \leq 5; -13 \leq k \leq 12; -11 \leq l \leq 12$
b (Å)	8.2818(17)	Reflections collected	3220
c (Å)	12.595(3)	Independent reflections	2189
β (°)	100.20(3)°	Reflections theta (°)	2.26 to 28.27
Volume	1191.69(645)	Absorption correction transmission	0.9444 to 0.9866
Z	4	Reflections with $I \geq 2\sigma(I)$	1427
Density (mg/m ³)	1.37251	Number of parameters	109
Absorption coefficient	0.115	Goodness-of-fit on F^2	1.006
F (000)	166	Final R indices [$I > 2s(I)$]	$R1 = 0.1884; wR2 = 0.1323$
Crystal size (mm ³)	$0.21 \times 0.25 \times 0.30$	R indices (all data)	$R1 = 0.0674; wR2 = 0.1027$
Theta range for data collection (°)	1.9 to 27.3	Refine different density	-0.224 to 0.176

TABLE-2
ATOMIC COORDINATES (IN Å²) OF 1-(MORPHOLINOMETHYL)INDOLINE-2,3-DIONE

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
N2	0.91766(9)	0.23385(12)	0.11391(8)	C1	0.70789(11)	0.30626(15)	-0.1031(1)
N1	0.73127(8)	0.33226(11)	0.00535(8)	C3	0.56961(11)	0.70484(16)	-0.05764(11)
C7	0.68098(9)	0.48053(14)	0.03062(9)	H3A	0.53110	0.75570	-0.11970
O2	0.59676(8)	0.46330(13)	-0.24949(7)	C13	0.95237(11)	0.37262(17)	0.18371(11)
C10	0.98088(11)	0.23531(16)	0.02322(11)	H13A	0.91260	0.36920	0.24520
H10A	0.95910	0.33020	-0.02090	H13B	0.93030	0.47180	0.14430
H10B	0.96040	0.14040	-0.02120	C4	0.57469(12)	0.77531(16)	0.04263(12)
O3	1.14402(7)	0.37200(13)	0.13337(9)	H4A	0.54030	0.87570	0.04810
O1	0.73752(10)	0.19019(12)	-0.15122(8)	C12	1.08328(12)	0.3691(2)	0.22195(12)
C6	0.68346(10)	0.54811(15)	0.13085(10)	H12A	1.10650	0.46160	0.26800
H6A	0.71920	0.49570	0.19340	H12B	1.10430	0.27210	0.26420
C8	0.62332(10)	0.55651(14)	-0.06320(9)	C11	1.11103(11)	0.23690(17)	0.06581(12)
C2	0.63447(10)	0.45189(15)	-0.15409(10)	H11A	1.13290	0.13850	0.10620
C9	0.79252(11)	0.21364(15)	0.08256(11)	H11B	1.15290	0.23970	0.00570
C5	0.63034(11)	0.69807(15)	0.13481(11)	H9A	0.7745(10)	0.1067(17)	0.0422(11)
H5A	0.63230	0.74770	0.20140	H9B	0.7566(11)	0.2191(14)	0.1471(11)

TABLE-3
INTERMOLECULAR HYDROGEN BONDS PARAMETERS OF 1-(MORPHOLINOMETHYL)INDOLINE-2,3-DIONE

D-H...A	D-H	H...A	D...A	D-H...A
C6-H6A-O1 ⁱ	0.9300	2.4700	3.349(2)	158.000
C5-H5A-O2 ⁱⁱ	0.9300	2.5200	3.216(2)	131.000

*Symmetry codes: (i) $x, 0.5-y, 0.5+z$; (ii) $x, 1.5-y, 0.5+z$

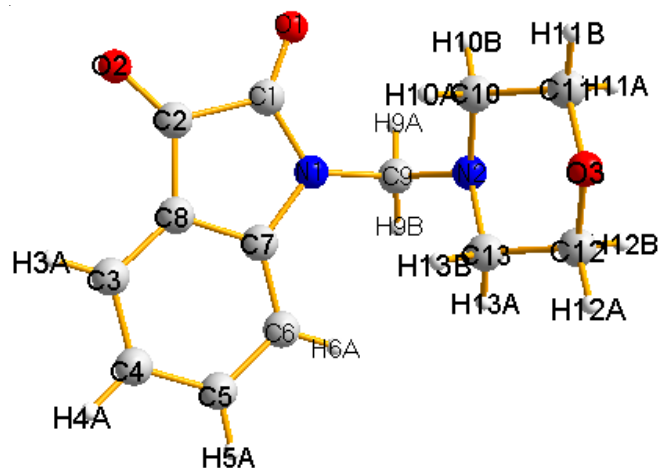


Fig. 1. Molecular structure of 1-(morpholinomethyl)indoline-2,3-dione

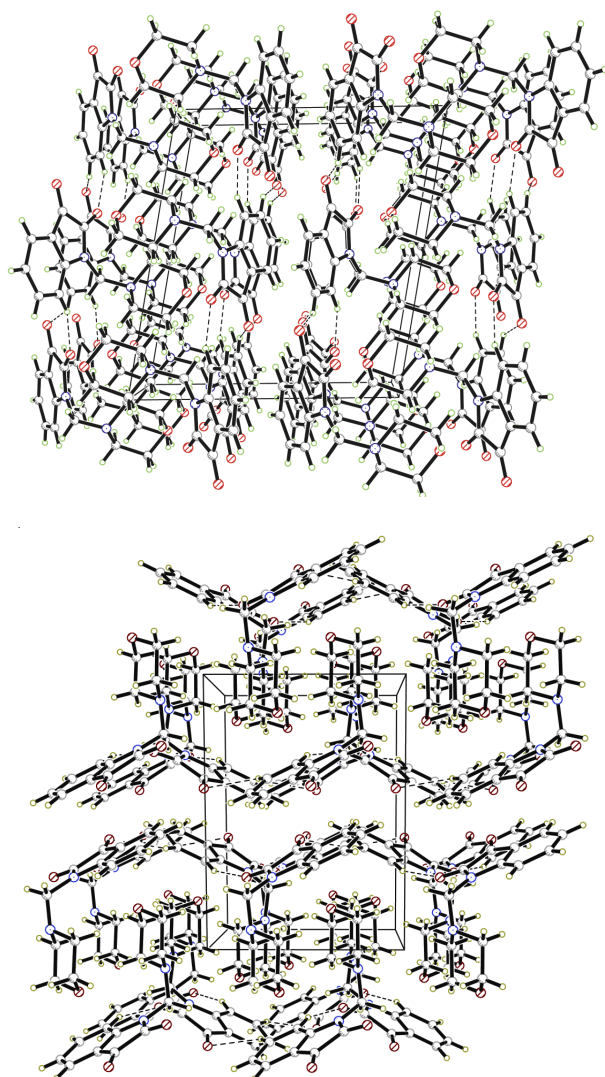


Fig. 2. Packing diagram of 1-(morpholinomethyl)indoline-2,3-dione

material due to a loss of cross-sectional area, it can be the shattering of a metal due to hydrogen embrittlement, or it can be the cracking of a polymer due to sunlight exposure. The use of corrosion inhibitors has been considered as the most effective method for the protection against such acid attack. Some inhibitors, such as imidazoline, Mannich base, Schiff base and some other heterocyclic compounds, have been employed in this process, but the concentration or the price is too high to be acceptable.

In the following work, the performance of the title compound as an inhibitor with the concentration from 100 to 1000 mg/L in 1M and 2M HCl under the temperature from 30 to 65 °C and the results were summarized in Table-4. From the table, it was found that almost all the inhibition efficiency increases along with the concentration of inhibitor, but there is difference in the two concentrations and different temperatures and it reaches to 81.9 % with the concentration of 1000 mg/L in 1 M HCl solution, further increase of the inhibitor does not increase the inhibition efficiency.

TABLE-4
CORROSION INHIBITION EFFICIENCY OF
1-(MORPHOLINOMETHYL)INDOLINE-2,3-DIONE

Concentration (mg/L)	HCl Concentration (M)	Temperature (°C)	Inhibition Efficiency (%)
100	1	30	13.8
100	1	45	27.9
100	1	60	21.3
100	2	30	18.2
100	2	45	19.0
100	2	60	16.7
200	1	30	23.5
200	1	45	27.9
200	1	60	33.3
200	2	30	26.3
200	2	45	23.1
200	2	60	20.8
500	1	30	55.8
500	1	45	69.8
500	1	60	66.7
500	2	30	53.1
500	2	45	63.7
500	2	60	58.8
1000	1	30	81.9
1000	1	45	77.5
1000	1	60	78.0
1000	2	30	72.9
1000	2	45	71.0
1000	2	60	60.0

The inhibition mechanism of the corrosion inhibiting may be mainly contributed to the adsorption. The process of adsorption is governed by the chemical structure of these inhibitors. The presence of N, O, S atoms and conjugated bonds in the structures makes the formation of *p-d* bonds resulting form

the overlap of p electrons to the $3d$ vacant orbital of Fe atoms, which conforms the adsorption of the compounds on the metal surface²¹. The inhibitive performance of 1-(morpholinomethyl)indoline-2,3-dione can be explained on the presence of polydentate nitron and indolin which rises the possibility of transferring the unshared electron of this molecule to iron²². The possible reaction centers are unshared electron pair of heteroatoms and/or π -electrons of aromatic ring. The schematic illustration of different modes of adsorption on metal is shown in Fig. 3.

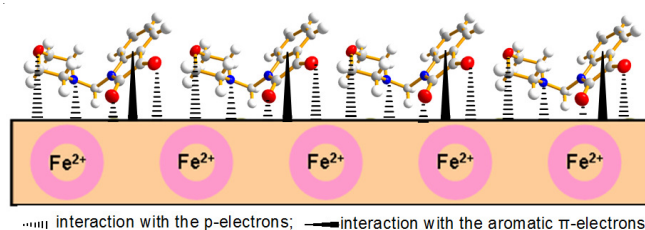


Fig. 3. Absorption of 1-(morpholinomethyl)indoline-2,3-dione molecules on the ion surface

Bioactivity: Microbiologically influenced corrosion (MIC) caused by growth of sulfate reducing bacteria (SRB), iron bacteria (IB) and total general bacteria (TGB) in oil pipelines, is considered a major problem for water treatment in the oil industry. Microbiologically influenced corrosion can result in different types of attack: pitting, crevices, dealloying and erosion in pipelines¹⁷. Corrosion products produced by microorganisms are production of hydrogen sulfide, molecular hydrogen, hydrogen ions and destabilization of metal oxide films. In addition, microbial degradation of crude oil can lead to increased acidity in the oil phase and oil containing acids is a problem concerning corrosion of pipelines. The reported results showed that the interaction of IB, SRB and TGB accelerated the corrosion rate and the corrosion in the mixture of IB, SRB and TGB was more serious than in a single microbial system. Different treatment system to inhibit corrosion should be considered, among which bactericide agent has received the greatest acceptance. Currently, oxidizer, aldehyde, quaternary ammonium salt and heterocycle compounds has been used as bactericide agents and Cl_2 , ClO_2 , formaldehyde, pentane-1,5-dial, trichloroisocyanuric acid (TCCA), etc.¹⁸, but the toxicity tests have been conducted on a limited selection. The antifungal activity of 1-(morpholinomethyl)-indoline-2,3-dione against oil field microorganism was tested under the concentration of 0.20 and 0.02 g/L and the results were summarized in Table-5. From the table, it can be found that

TABLE-5
ANTIFUNGAL ACTIVITY OF 1-(MORPHOLINOMETHYL)-
INDOLINE-2,3-DIONE AGAINST OILFIELD
WATER-BORNE BACTERIA

Concentration	Microbiotic concentration/mL		
	SIB	IB	TGB
-	110.0	110.0	110.0
0.20 g/L	0.0	0.0	70.0
0.02 g/L	25.0	25.0	110.0

1-(morpholinomethyl)indoline-2,3-dione is antifungal active against SRB and IB, but inactive against TGB under both concentrations.

Conclusion

1-(Morpholinomethyl)indoline-2,3-dione was synthesized and the its anticorrosion characters and the mechanism on the corrosion of high protective Q235A steel in HCl solution were screened and discussed. The title compound can inhibit the corrosion with moderate inhibition efficiency in different conditions and the highest reaches to 81.9 % in 1M HCl with the concentration of 1000 mg/L. Besides, it displays potent activity against the oilfield water-borne bacteria, especially for SRB and IB.

ACKNOWLEDGEMENTS

This work was financially supported by Scientific Research Program Funded by Shaanxi Provincial Education Department (12JK0589).

REFERENCES

1. M. Yoshikawa, T. Murakami, A. Kishi, T. Sakurama, H. Matsuda, M. Nomura, H. Matsuda and M. Kubo, *Chem. Pharm. Bull. (Tokyo)*, **46**, 886 (1998).
2. G. Chen and X.J. Hao, *Nat. Prod. Res. Dev.*, **22**, 356 (2010).
3. G. Chen, X.J. Hao, Q.Y. Sun and J. Ding, *Chemical Papers*, **64**, 673 (2010).
4. G. Chen, H.P. He, J. Ding and X.J. Hao, *Heterocycl. Commun.*, **15**, 355 (2009).
5. G. Chen, J. Yang, S. Gao, H.P. He, S.L. Li, Y.T. Di, Y. Chang, Y. Lu and X.J. Hao, *Mol. Divers.*, **16**, 151 (2012).
6. G. Chen, Y. Tang, J. Zhang, Y. Wu, X.-J. Hao and S.-Z. Mu, *Lett. Org. Chem.*, **8**, 614 (2011).
7. M.A. Quraishi and H.K. Sharma, *Mater. Chem. Phys.*, **78**, 18 (2003).
8. H. Ju, Z.-P. Kai and Y. Li, *Corros. Sci.*, **50**, 865 (2008).
9. K.M. Ismail, *Electrochim. Acta*, **52**, 7811 (2007).
10. M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. El Kadiri, B. Hammouti and M. Benkaddour, *Mater. Chem. Phys.*, **105**, 373 (2007).
11. N. Soltani, M. Behpour, S.M. Ghoreishi and H. Naeimi, *Corros. Sci.*, **52**, 1351 (2010).
12. G. Quartarone, T. Bellomi and A. Zingales, *Corros. Sci.*, **45**, 715 (2003).
13. S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan and G. Bouet, *Corros. Sci.*, **53**, 1484 (2011).
14. J. Fang and J. Li, *J. Mol. Struct. THEOCHEM*, **593**, 179 (2002).
15. M. Behpour, S.M. Ghoreishi, N. Soltani and M. Salavati-Niasari, *Corros. Sci.*, **51**, 1073 (2009).
16. A. Yurt, A. Balaban, S.U. Kandemir, G. Bereket and B. Erk, *Mater. Chem. Phys.*, **85**, 420 (2004).
17. K. Stanly Jacob and G. Parameswaran, *Corros. Sci.*, **52**, 224 (2010).
18. G. Chen, H. Su, Y. Song, Y. Gao, J. Zhang, X. Hao and J. Zhao, *Res. Chem. Intermed.*, **39**, 3669 (2013).
19. M.A. Quraishi, I. Ahamad, A.K. Singh, S.K. Shukla, B. Lal and V. Singh, *Mater. Chem. Phys.*, **112**, 1035 (2008).
20. I. Ahamad, R. Prasad and M.A. Quraishi, *Corros. Sci.*, **52**, 1472 (2010).
21. A. Visa, M. Mracec, B. Maranescu, V. Maranescu, G. Ilia, A. Popa and M. Mracec, *Chem. Cent. J.*, **6**, 91 (2012).
22. G. Chen, Y. Wang, H.P. He, S.L. Li, L.G. Zhou and X.J. Hao, *Acta Botany Yunnan*, **29**, 712 (2007).