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Synthesis, Structure and Anticorrosion of 1-Methyl-indolin-2-one-3-oxime

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1-Methyl-indolin-2-one-3-oxime, was synthesized and analyzed by X-ray single crystal analysis. There are three independent 3-hydroxyimino-1-methylindolin-2-one molecules and a water molecule in the asymmetric unit. The inhibition and the mechanism of 3-hydroxyimino-1-methylindolin-2-one on the corrosion of N80 steel in HCl solution were screened. The results showed that 3-hydroxyimino-1-methylindolin-2-one 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.

Keywords: Isatin, Corrosion inhibition, Adsorption.

INTRODUCTION

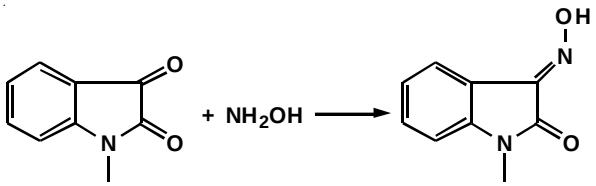
Isatin, 1*H*-indole-2,3-dione, is an important indole derivative, which was first obtained by Erdmann and Laurent in 1841 as a product from the oxidation of indigo dye by nitric acid and chromic acids. The compound is found in many plants, such as *Isatis tinctoria*, *Calanthe discolor*, *Strobilanthes cusia* (Nees) Kuntze and *Couroupita guianensis Aubl.*, even in mammalian tissue[1,2]. It has versatile bioactivity and it is useful to synthesize a large variety of heterocyclic compounds in preparing drugs[3,4]. Isatin Schiff bases are reported to have antibacterial activity against *Bacillus subtilis*, Gram (+) and Gram (–) bacterial strains and *Magnaporthe grisea*[5,6] among others.

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 adsorption[9-11]. 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 molecules[12-14]. Some polydentate Schiff base compounds (PSCs) have been reported as effective corrosion inhibitors for various metals in acid media[13,15-17]. Several isatin derivatives have been reported as inhibitors in HCl solution[18-22]. 1-Methyl-indolin-2-one-3-oxime, a related structure, was synthesized by a condensation reaction of N-methyl isatin and hydroxylamine. In this paper we report the X-ray crystal structure of the 1-methyl-indolin-2-one-3-oxime, a related derivative of these bioactive compounds.

EXPERIMENTAL

Synthesis of 1-methyl-indolin-2-one-3-oxime: N-Methyl isatin (1 mmol) was dissolved in methanol (20 mL), 10 mL me thanol solution of 1.2 mmol hydroxylamine was added dropwise, until the disappearance of isatin, 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 = 3:1), giving the desired compound. 20 mg of the compound was dissolved in 30 mL methanol and the solution was kept at room temperature for 5 d, natural evaporation gave yellow single crystals 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-methods[13] and refined by a full-matrix least squares 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-I** 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 geometrically and allowed to ride on their parent



Scheme-I: Synthesis of 1-methyl-indolin-2-one-3-oxime

atoms, with d(N-H) = 0.86 Å and Uiso(H) = 1.2 Ueq(N), d(C-H) = 0.93 or 0.96 (CH_3) Å and Uiso(H) = 1.2 Ueq(C) or 1.5 Ueq(C). Crystal data and refinement details were given in Table-1.

Gravimetric measurements: The corrosion tests were performed on N80 steel with a composition (in wt.%) C: 0.20, P: 0.015, Si: 1.45, S: 0.15, Mn: 0.020 and Fe balance. The electrolyte solution was prepared from analytical grade 38 % HCl and distilled water. The concentration range of 1-methyl-indolin-2-one-3-oxime was employed as 100 mg/L and 1000 mg/L. All tests have been performed in deaerated solutions at 60 ± 0.5 ºC. 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.

RESULTS AND DISCUSSION

Structure: The X-ray structural analysis confirmed the assignment of its structure from spectroscopic data. Geometric parameters of 1-methyl-indolin-2-one-3-oxime are in the usual ranges. The atomic coordinates are displayed in Table-2 and the molecular structure is depicted in Fig. 1. The space-group is P-1(2) with a triclinic crystal system. There are three independent 3-hydroxyimino-1-methylindolin-2-one molecules and a water molecule in the asymmetric unit. The crystal packing is stablized by O-H and O and O-H and N hydrogen bonds between 3-hydroxyimino-1-methylindolin-2-one molecules and the water molecule as shown in Fig. 2 and the hydrogen bonds parameters are included in Table-3. The water molecule bonds with three 3-hydroxyimino-1-methylindolin-2-one molecules through four hydrogen bonds, while the hydrogen bonds of three 3-hydroxyimino-1-methylindolin-2-one molecules are quite different. The weak π-π stacking interactions [centroid–centroid distances in the range 3.446(2)-3.983(2) Å], associated with the hydrogen bonds forming a two-dimensional network as shown in Fig. 3.

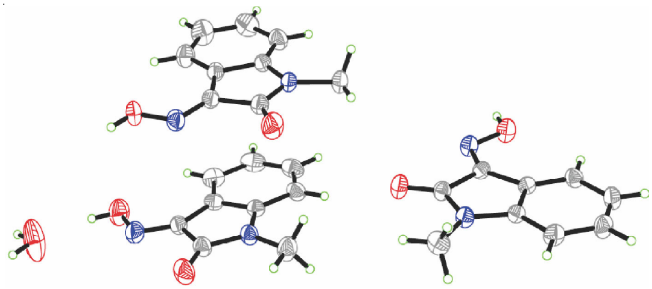


Fig. 1. Molecular structure of tri-1-methyl-indolin-2-one-3-oxime monohydrate

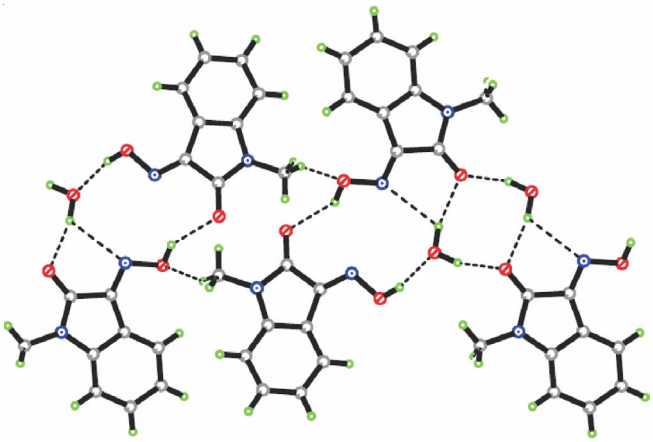


Fig. 2. Intermolecular hydrogen bonds of 1-methyl-indolin-2-one-3-oxime

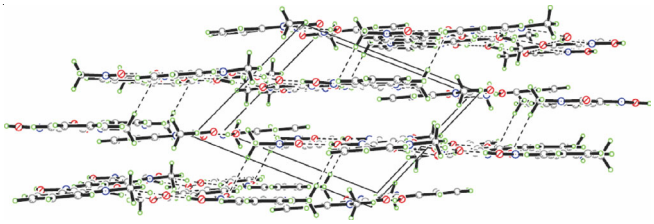


Fig. 3. Packing diagram of 1-methyl-indolin-2-one-3-oxime

Inhibitor properties and mechanism: Corrosion is the gradual destruction of materials (usually metals) by chemical reaction with its environment. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Because

TABLE-1
EXPERIMENTAL DATA OF 1-METHYL-INDOLIN-2-ONE-3-OXIME

Crystal parameter	Data	Crystal parameter	Data
a (Å)	8.920(3)	Index ranges	$-4 \le h \le 5$; $-13 \le k \le 12$; $-11 \le l \le 12$
b (Å)	10.811(4)	Reflections collected	3325
c (Å)	14.915(5)	Independent reflections	2367
α (º)	91.33(0)	Reflections theta (°)	2.25-28.25
β (º)	101.01(0)	Absorption correction transmission	0.9450-0.9850
γ (º)	112.78(0)	Reflections with $I \ge 2\sigma(I)$	1420
Volume	1294.12(215)	Number of parameters	110
Z	2	Goodness-of-fit on F^2	1.006
Density (mg/m^3)	1.510	Final R indices [$I \ge 2\sigma(I)$]	$R_1 = 0.1882$; $wR_2 = 0.1322$
Absorption coefficient	0.113	R indices (all data)	$R1 = 0.0675$; $wR_2 = 0.1028$
$F_{(000)}$	168	Refine different density	-0.224 to 0.176
Crystal size (mm^3)	0.22 × 0.25 × 0.30	Theta range for data collection (º)	1.9-27.3

TABLE-2
ATOMIC COORDINATES (IN Å^2) OF 1-METHYL-INDOLIN-2-ONE-3-OXIME

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
C1	1.0271(3)	-0.0706(3)	0.09769(15)	H19A	0.60850	-0.03360	0.25720
H1C	0.97740	-0.00600	0.09080	H19B	0.50850	-0.06820	0.33550
H1D	0.95270	-0.15390	0.06140	H19C	0.68220	0.05400	0.35280
H1E	1.13020	-0.03660	0.07740	C20	0.4430(3)	0.1584(3)	0.42273(17)
C2	1.1891(3)	-0.2589(2)	0.18264(15)	H20A	0.48500	0.10370	0.45700
H2A	1.18520	-0.25680	0.12000	C21	0.3780(4)	0.2375(3)	0.4624(2)
C3	1.2550(3)	-0.3391(2)	0.23265(16)	H21A	0.37650	0.23600	0.52450
H3A	1.29590	-0.39190	0.20300	C22	0.3155(4)	0.3182(3)	0.4117(2)
C4	1.2614(3)	-0.3426(2)	0.32544(16)	H22A	0.27120	0.36960	0.43990
H4A	1.30740	-0.39670	0.35760	C23	0.3178(3)	0.3241(2)	0.31945(18)
C5	1.1999(3)	-0.2663(2)	0.37148(15)	H23A	0.27650	0.37960	0.28560
H5A	1.20320	-0.26940	0.43410	C24	0.4038(3)	0.2266(2)	0.18659(15)
C6	1.0575(2)	-0.0964(2)	0.34600(13)	C25	0.4784(3)	0.1244(2)	0.18822(17)
C7	1.0105(3)	-0.0384(2)	0.25993(14)	C26	0.4435(3)	0.1635(2)	0.33104(15)
C8	1.1296(2)	-0.18248(19)	0.22847(13)	C27	0.3819(3)	0.2464(2)	0.27895(15)
C9	1.1338(2)	-0.18576(19)	0.32271(13)	N1	1.0252(2)	-0.05933(18)	0.41960(11)
C10	0.8968(3)	0.2792(3)	0.09247(17)	N2	1.0588(2)	-0.09364(18)	0.19319(11)
H10A	0.88650	0.28120	0.02730	N3	0.6924(2)	0.6279(2)	0.10394(15)
H10B	0.82900	0.19060	0.10500	N4	0.8424(2)	0.37665(18)	0.12804(12)
H10C	1.01110	0.30120	0.12150	N5	0.3804(2)	0.27722(18)	0.11122(13)
C11	0.7880(3)	0.4583(2)	0.07539(15)	N6	0.5003(2)	0.09227(17)	0.27555(13)
C12	0.7441(3)	0.5409(2)	0.13851(16)	O1	1.0755(2)	-0.11735(17)	0.4950(1)
C13	0.7619(3)	0.5382(2)	0.31557(18)	H1B	1.05260	-0.09080	0.54040
H13A	0.72030	0.60350	0.32350	O2	0.9441(2)	0.04077(16)	0.25021(11)
C14	0.8102(3)	0.4762(3)	0.38937(18)	O3	0.6579(2)	0.69901(18)	0.16874(15)
H14A	0.80170	0.50100	0.44770	H3C	0.62970	0.75640	0.14480
C15	0.8700(3)	0.3796(3)	0.37811(17)	O4	0.7795(2)	0.46187(18)	-0.00736(11)
H15A	0.90100	0.33990	0.42910	O5	0.3164(2)	0.37245(16)	0.12083(12)
C16	0.8857(3)	0.3390(2)	0.29342(15)	H5C	0.30170	0.40300	0.07160
H16A	0.92630	0.27300	0.28610	O6	0.5143(2)	0.07832(18)	0.12371(13)
C17	0.7775(3)	0.5000(2)	0.22938(15)	O7W	0.5777(4)	0.8629(2)	0.06685(15)
C18	0.8386(2)	0.4006(2)	0.22021(14)	H7WA	0.56130	0.93410	0.09770
C19	0.5818(3)	0.0036(2)	0.3080(2)	H7WB	0.55200	0.86830	0.00190

corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. 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 3-hydroxy-imino-1-methylindolin-2-one as an inhibitor with the concentration from 100-1000 mg/L in 1 M and 2 M HCl under the temperature from 30-60 ºC and the results were summarized in Table-4. From the table, it was found that almost all the inhibition efficiency (IE) increases along with the concentration of inhibiter and it reaches to 81.5 % with the concentration of 1000 mg/L in 1M HCl solution at 60 ºC, further increase of the inhibitor does not increase the IE.

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 3*d* vacant orbital of Fe atoms, which conforms the adsorption of the compounds on the metal surface[23]. The inhibitive performance of 1-methyl-indolin-2-one-3-oxime can be explained on the presence of polydentate Schiff base and indolin which raises the possibility of transferring the unshared electron of this molecule to iron[24]. The molecules may absorb on the ion surface by the coordinate covalent bonds with the 3*d* vacant orbital of Fe atoms in the manner described in Fig. 1 to form the protective film. The possible reaction centers are unshared electron pair of hetero-atoms and/or *p*-electrons of aromatic ring. The schematic illustration of different modes of adsorption on metal is shown in Fig. 4.

TABLE-3
INTERMOLECULAR HYDROGEN BONDS PARAMETERS OF 1-METHYL-INDOLIN-2-ONE-3-OXIME

D-H···A	D-H	H···A	D···A	D-H···A
O7W-H7WA-O6^{i}	0.9600	1.8200	2.752(3)	164.000
O1-H1B-N1^{ii}	0.8200	2.1100	2.780(3)	139.000
O7W-H7WB-O6^{iii}	0.9600	2.0200	2.958(3)	165.000
O7W-H7WB-N5^{iii}	0.9600	2.5900	3.181(3)	120.000
O3-H3C-O7W	0.8200	1.7800	2.579(3)	165.000
O5-H5C-O4^{iv}	0.8200	2.0500	2.753(3)	144.000

*Symmetry codes: (i) x, 1+y, z; (ii) 2-x, -y, 1-z; (iii) 1-x, 1-y, -z; (iv) 0, 0, 0.

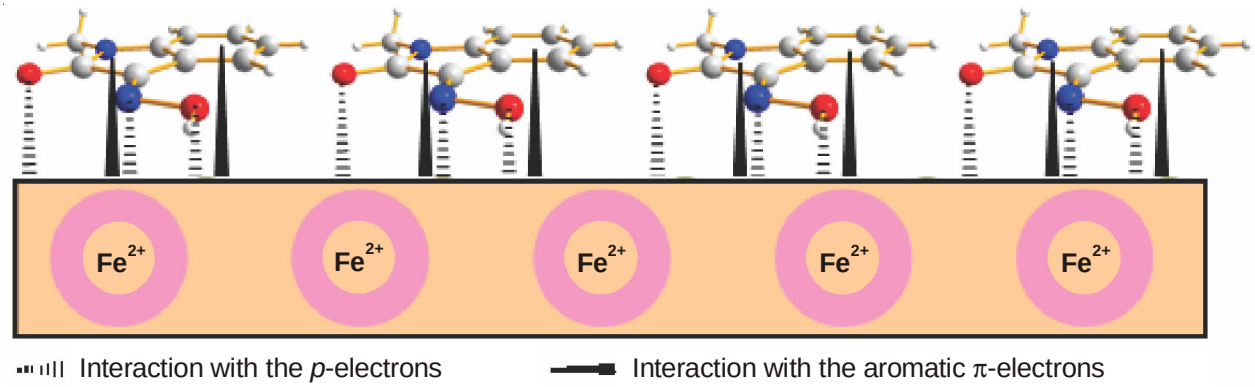


Fig. 4. Absorption of 1-methyl-indolin-2-one-3-oxime molecules on the iron surface

TABLE-4
CORROSION INHIBITION EFFICIENCY OF 1-METHYL-INDOLIN-2-ONE-3-OXIME

Concentration (mg/L)	HCl conc. (M)	Temperature (ºC)	Inhibition efficiency (%)
100	1	30	15.2
100	1	45	27.8
100	1	60	30.2
100	2	30	18.9
100	2	45	19.8
100	2	60	29.0
200	1	30	29.7
200	1	45	33.2
200	1	60	35.5
200	2	30	21.5
200	2	45	26.9
200	2	60	28.8
500	1	30	45.2
500	1	45	66.3
500	1	60	72.5
500	2	30	44.8
500	2	45	60.0
500	2	60	68.9
1000	1	30	68.2
1000	1	45	73.1.9
1000	1	60	81.5
1000	2	30	63.7
1000	2	45	69.3
1000	2	60	70.4

Conclusion

1-Methyl-indolin-2-one-3-oxime was synthesized and the inhibition and the mechanism on the corrosion of high protective N80 steel in HCl solution were screened and discussed. It can inhibit the corrosion with moderate inhibition efficiency in different conditions and the highest reaches to 81.5 % with the concentration of 1000 mg/L in 1 M HCl solution.

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