

## Synthesis and Mechanochemical Synthesis of *N, N'*-bis (2-thienylethyl)-2,3-butanediimine with corrosion inhibitor properties

Liliana Hernández Perales<sup>1a</sup>, Christiaan Jardínez<sup>1b</sup>,  
Rosa A. Vázquez García<sup>1c\*</sup>, Oscar Coreño Alonso<sup>2d</sup>,  
M. Aurora Veloz Rodríguez<sup>1e</sup>, Julián Cruz Borbolla<sup>1f</sup>, Juan Coreño Alonso<sup>1g</sup>,  
Thangarasu Pandiyan<sup>3h</sup>, Leticia E. Hernández Cruz<sup>1i</sup>,  
Marcos Martínez García<sup>3j1</sup>

<sup>1</sup>Universidad Autónoma del Estado de Hidalgo. Área Académica de Ciencias de la Tierra y Materiales y Área Académica de Química. Cd. Universitaria, C.P. 42184, Pachuca, Hgo., México.

<sup>2</sup>Depto. Ing. Civil, Universidad de Guanajuato, Juárez 77 C. P. 36000.

<sup>3</sup>Facultad de Química e Instituto de Química, UNAM, Cd. Universitaria, Circuito exterior, Coyoacán, C.P. 04510, México D.F.

<sup>a</sup>lhperales@gmail.com, <sup>b</sup>chrisjv\_18@live.com, <sup>c</sup>rosavg@uaeh.edu.mx, <sup>d</sup>ocoreno@yahoo.com, <sup>e</sup>maveloz70@yahoo.com.mx, <sup>f</sup>jcruzborbolla@yahoo.com.mx, <sup>g</sup>jcorenoalonso@gmail.com, <sup>h</sup>pandiyan61@yahoo.com, <sup>i</sup>laetitia106@hotmail.com, <sup>j</sup>margar@unam.mx.

**Keywords:**  $\alpha$ -diimines; inhibitors; corrosion; electrochemical; DFT.

**Abstract.** In this work, we report the conventional and mechanochemical synthesis of the  $\alpha$ -diimine derivate of 2, 3-butanedione and the primary amine 2-aminoethanethiol designated DD-DC and DD-DC/MS respectively. The products were characterized by <sup>1</sup>H and <sup>13</sup>C-NMR, FT-IR, MS-EI and elemental analysis. The products were also electrochemically evaluated by potentiodynamic polarization technique in order to measure their corrosion inhibition efficiency on AISI 1018 steel, immersed in a corrosive solution type NACE TM 0177. The results indicate that the compound obtained under mechanochemical synthesis conditions, DD-DC/MS, presents better inhibitory properties with 53% efficiency at 10 ppm concentration. On the other hand, the compound obtained by conventional synthesis (DD-DC) presented efficiency of 29% at 10 ppm concentration. Also, the DFT results show that  $\alpha$ -diimine derivatives possesses corrosion inhibition properties, consisting of the transfer of high-charge density which in the delocalization region (N=C-C=N) is formed by  $\pi$  (C=N) and SH, these moiety play an important role, because their electron lone pairs help to form a protective coating to form an adsorption layer. The results showed that cysteamine compound turns out to be a good corrosion inhibitor for the steel iron surface in an acid medium forming an adsorption film over metallic surface.

### Introduction

Development of corrosion inhibitors based on organic compounds containing sulfur, nitrogen or oxygen atoms is being of great interest in the field of corrosion related to the chemical industry because of their great utility in protecting carbon steel, which commonly used in the transport of fluids in the petroleum industry [1-3]. It is noteworthy that the efficiency of organic inhibitors depends on the nature of the material, the state of the metallic surface, and the chemical composition and structure of the inhibitor [4-6]. Furthermore, the stability of adsorption layer formed by organic inhibitors on the metal surface is also important in the corrosion inhibition as it depends on the physicochemical properties of the molecule. The adsorption properties of the compounds are mostly associated with the existence of functional groups, steric effects, type of

corrosive environment, the nature of the interaction of  $\pi$  orbitals from the inhibitor with the metal orbitals, and the method of compound synthesis [7,8]. Thus, in this paper, a novel synthesis method is employed to obtain  $\alpha$ -diimine compounds having SH as polar ends. The electrochemical properties of the compounds were analyzed in order to use as corrosion inhibitors for the iron steel surface; in addition, a relationship between the corrosion inhibition efficiency and the structure of compounds is also analyzed.

## Experimental Section

The reagents were used as purchased from Sigma-Aldrich without further purification. For all the compounds, Infrared spectra were recorded on Nicolet FT-IR Magna 550 in pellets (KBr);  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on Varian-Unity-300 MHz equipment with  $\text{CD}_3\text{OD}$  as solvent. Mass spectra were measured on a mass spectrometer Jeol JMS AX505HA ( $\text{M}^+$ ). Elemental analysis data were obtained using Perkin Elmer model 2400 equipment. The electrochemical evaluation was carried out using a Potentiostat-Galvanostat AUTO-LAB model PGSTAT30, coupled to a computer having General Purpose Electrochemical System (GPES) software. For the compounds synthesized, the polarization curves were obtained using different concentrations (10, 25, 50 and 100 ppm).

### Synthesis of *N, N'*-bis (2-thylenylethyl)-2,3-butanodiimine (DD-DC).

In a 100 mL round-bottomed flask, 1.47 mL (17 mmol) of 2,3-butanodione was first dissolved in methanol (50 mL), and then 3 drops of formic acid (98%) and 2.85 g (37 mmol) of 2-aminoethanethiol were added. The resulting reaction mixture was stirred for 24 hours at room temperature under argon atmosphere. The reaction was monitored by thin layer chromatography by using  $\text{Al}_2\text{O}_3$  plates. After the reaction was over, the resulted product was dried at vacuum. Product (oily, purple color): Yield (2.9 g, 82.16%). b.p.: 222 °C. IR (Film,  $\text{cm}^{-1}$ ): 1650 (C=N), 2875 and 2923 (C-H aliphatic).  $^1\text{H}$ -RMN ( $\text{CD}_3\text{OD}$ , 300 MHz),  $\delta$ (ppm): 4.80 (b, 2H, SH), 3.55 (t, 4H,  $\text{CH}_2\text{-N}=\text{C}$ ), 3.5 (t, 4H,  $\text{CH}_2\text{-S}$ ), 2.84 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$ -RMN ( $\text{CD}_3\text{OD}$ , 75 MHz),  $\delta$ (ppm): 162.00, 39.83, 36.71, 29.77. MS-EI(m/z): 204 ( $\text{M}^+$ ). E.A.:  $\text{C}_8\text{H}_{16}\text{N}_2\text{S}_2$ ; Calculated % C= 47.06, % H= 7.84, % N= 13.72. Experimental. % C= 46.90, % H= 7.80, % N= 13.65.

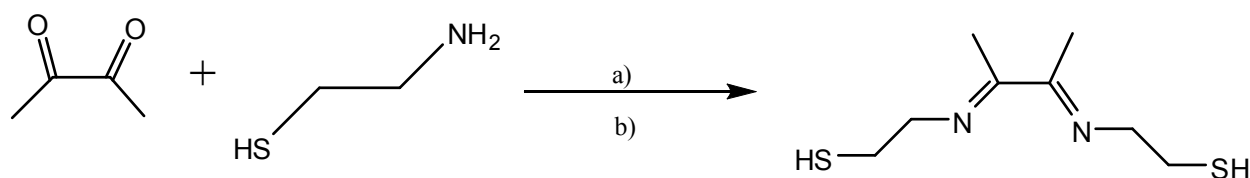
### Mechanosynthesis of *N, N'*-bis (2-thylenylethyl)-2,3-butanodiimine (DD-DC/MS).

In a vial containing 5 steel balls (8.3 g of each), the mixture of 1.47 mL (17 mmol) of 2,3-butanodione and 2.85 g (37 mmol) of 2-aminoethanethiol was allowed to react for 1.0 hour in a SPEX 8000D mixer-mill. The reaction was monitored by thin layer chromatography by using  $\text{Al}_2\text{O}_3$  plates. The product was extracted using methanol ( $\text{CH}_3\text{OH}$ ) and the product dissolved was filtered through alumina ( $\text{Al}_2\text{O}_3$ ). The resulted product was dried under vacuum. Product (oily, purple color):  $\text{C}_8\text{H}_{16}\text{N}_2\text{S}_2$ , Yield: (3.3 g, 93.48%), b.p.: 222 °C. IR (Film,  $\text{cm}^{-1}$ ): 1650 (C=N), 2875 and 2923 (C-H aliphatic).  $^1\text{H}$ -RMN ( $\text{CD}_3\text{OD}$ , 300 MHz),  $\delta$ (ppm): 4.80 (b, 2H, SH), 3.55 (t, 4H,  $\text{CH}_2\text{-N}=\text{C}$ ), 3.5 (t, 4H,  $\text{CH}_2\text{-SH}$ ), 2.84 (s, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$ -RMN ( $\text{CD}_3\text{OD}$ , 75 MHz),  $\delta$ (ppm): 162.00, 39.83, 36.71, 29.77. MS-EI (m/z): 204 ( $\text{M}^+$ ). E.A.:  $\text{C}_8\text{H}_{16}\text{N}_2\text{S}_2$ ; Calculated % C= 47.05, % H= 7.89, % N= 13.71. Experimental. % C= 46.95, % H= 7.82, % N= 13.69.

## Results and Discussion

### Synthesis and Mechanochemistry

The synthesis of the  $\alpha$ -diimine, DD-DC was carried out according to Fig. 1. The compound was synthesized by the condensation of 2,3-butanedione with 2-aminoethanethiol in methanol in the presence of formic acid as a catalyst. The product was isolated after 24 h of stirring under inert atmosphere. Product is oily, soluble in polar solvents. The compound was also synthesized using a mechanochemistry method (DD-DC/MS) in the absence of both solvent and catalyst.



Reagents and conditions: a) Conventional method: acid formic, stirred 24 hours. b) Mechanochemical synthesis method: Mill in a steel vial, 1 hour.

Fig. 1. General route for the  $\alpha$ -diimines synthesis DD-DC/MS and DD-DC.

The compounds were characterized spectroscopically ( $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , FT-IR and elemental analysis). The FT-IR spectra results showing that the presence of the imine group in the compounds by observing vibration bands in  $1650\text{ cm}^{-1}$  that correspond to  $\text{C}=\text{N}$  (Fig. 2).  $^{13}\text{C-RMN}$  spectrum of DD-DC/MS (Fig. 3) also shows the presence of  $\text{C}=\text{N}$  group which is considered as binding site for metal in the corrosion inhibition process. Although the different routes of synthesis were adopted for the compound, similar properties were observed in solution, but they were differed in the solid state, possibly associated with the formation of a predominant isomer *cis* or *trans* during the synthesis of the compound by mechanochemical synthesis method [9].

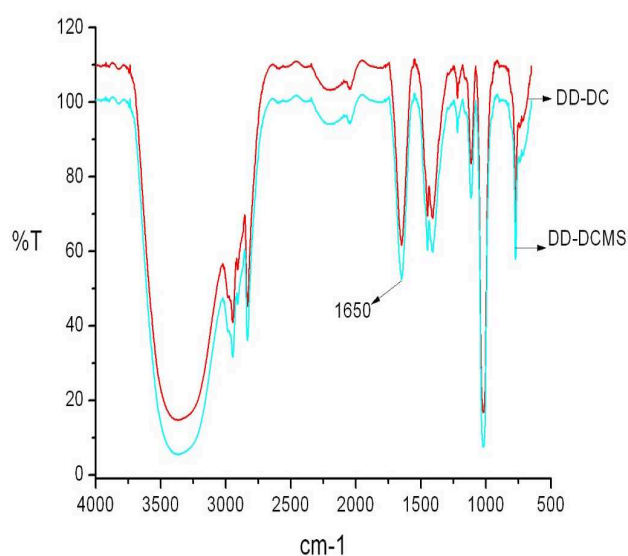


Fig. 2. FTIR spectra of  $\alpha$ -diimines synthesized by two different methods.

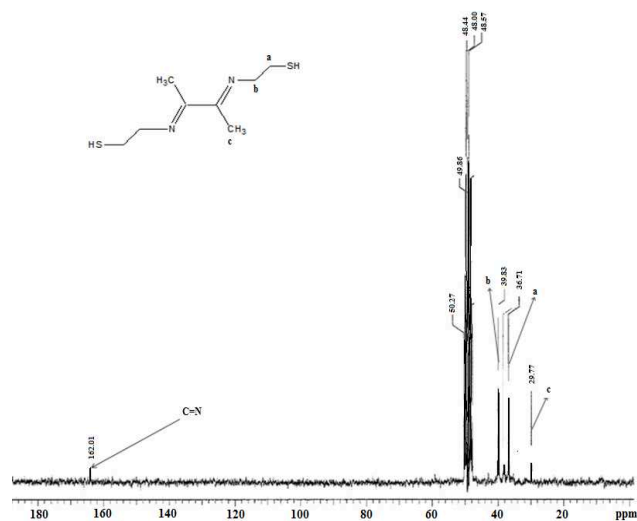


Fig. 3.  $^{13}\text{C-RMN}$  spectrum of DDC/MS in  $\text{CD}_3\text{OD}$ .

### Electrochemical Evaluation

The synthesized compounds through mechanochemical synthesis or by the conventional method were evaluated electrochemically to determine their corrosion inhibition efficiency. Electrochemical data (Table 1) obtained for compounds DD-DC and DD-DC/MS show that at the concentration of 10 ppm, there is a considerable decrease in oxidation currents; however, for higher potentials (0.08 to 0.15), the whole oxidation reaction of the system is favored at 25, 50 and 100 ppm, which is observed by the current values greater than the blank (Fig. 4 just for DD-DC/MS). In the cathodic reaction, it is noted that for all concentrations, a decrease in the reduction currents respect to the blank was observed, specifically at 10 ppm. In the corrosion inhibition analysis, for the corrosion parameters such as the corrosion potential, the presence of the compound does not show a significant difference. These values are very similar to the blank showing that the initial stage of corrosion inhibition process is very important and the same in both cases. However, the polarization resistance increases significantly after addition of the compounds in to the corrosion medium (with all the concentrations used); it relates the corrosion inhibition action on the metal surface.

Table 1. Corrosion inhibition parameters of the compounds at different concentrations (10, 25, 50 and 100 ppm).

Compound.	Concentration (ppm)	$E_{corr}$ (V)	$R_p$ ( $\Omega \text{ cm}^2$ )	%E
Blank	-	-0.5799	60	
	25	-0.5827	63	5
	50	-0.5797	68	12
	100	-0.5804	83	27
DD - DC	10	-0.5577	85	29
	25	-0.5629	86	30
	50	-0.5403	88	32
	100	-0.5415	98	39
DD-DC/MS	10	-0.5745	127	53
	25	-0.5798	112	47
	50	-0.5867	101	41
	100	-0.5939	105	43

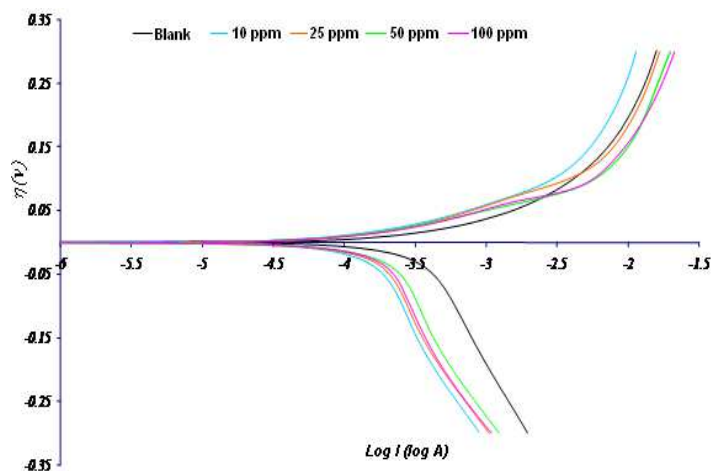


Fig. 4. Polarization curves obtained for AISI 1018 steel immersed in a corrosive solution type NACE TM 0177, in the absence and in presence of DD-DC/MS (10, 25, 50 and 100 ppm) with stirring (1000 rpm). The scan rate is  $0.1 \text{ mVs}^{-1}$ .

The Tafel slopes of the anodic process show that there are similarities in the main reactions occurred, although a slightly lower current is detected than that in the blank, relating high charge transfer caused by adsorptive processes of the compound on the metal surface. Furthermore, for DD-DC/MS, the cathodic slopes are also similar as the seen for DD-DC, indicating that the main process of the reduction reaction is not affected by the presence of the compound. This observation could be related to the diffusion process of the compound towards the metal surface. After analyzing the corrosion current (Table 1) and the Tafel slopes, for both compounds, it has been observed that DD-DC/MS compound shows the greater corrosion inhibition than that observed for DD-DC. Finally, the corrosion efficiency (%) shows that DD-DC/MS compound exhibits a greater corrosion inhibition, about 50 %, at 10 ppm than DD-DC compound. It is important because it is noticed that the synthesis method affects also the inhibitory properties of the compound. This could be attributed to the spatial ordering achieved through mechanosynthesis. In order to corroborate it, DFT studies were performed to the compound in its *cis* and *trans* configurations.

### DFT Theoretical Studies

Modeling and optimization of the  $\alpha$ -diimine structure DD-DC were studied by a quantum mechanical method that applying density functional theory (DFT) using the Gaussian 09 [10], The B3LYP [11, 12] exchanges-correlation functional was employed, with the basis set 6-31G\*\* for all atoms. For the molecule, a vibrational analysis was performed in order to find out the optimized geometries correspond to a minimum in the potential energy curve, because all the frequencies were positive, and in an aqueous medium (dielectric constant =78.39) by means of the PCM method [13]. The parameters of the chemical descriptors (Table 2) indicate that there is a strong influence on the chemical reactivity of the compound by the presence of sulfur atoms in the compound, the molecule can react with the metal surface efficiently as it has a higher HOMO value. Furthermore, the modeling of the electronic structures of the  $\alpha$ -diimine shows that the HOMO orbital is mainly located on the sulphur atom (see Fig. 5). The parameters obtained for the *trans* and *cis* configuration

of the compound show that there is also a contribution from the  $\sigma$  orbitals of the systems, suggesting that the sulfur atoms could be considered as the reactive site for the metal surface adsorption, the results of the difference of total energy obtained with DFT shows that the *trans* molecules are more stable than the *cis* ones, For DD-DC system there is energy difference of 12.30 kcal/mol, which is higher in aqueous phase than the gas phase, because in the former a mixture of both of the species is present.

Table 2. DFT parameters of the compounds.				
In the gas phase				
Molecule	$E_{(HOMO)}$ (eV)	$E_{(LUMO)}$ (eV)	Dipole (Debye)	Log P
DD-DC				
<i>trans</i>	-6.53	-1.36	0.42	2.03
<i>cis</i>	-6.26	-1.36	2.17	2.03
In the water as solvent				
Molecule	$E_{(HOMO)}$ (eV)	$E_{(LUMO)}$ (eV)	Dipole (Debye)	Log P
DD-DC				
<i>trans</i>	-6.5	-1.37	0.45	2.03
<i>cis</i>	-6.3	-1.46	2.17	2.03

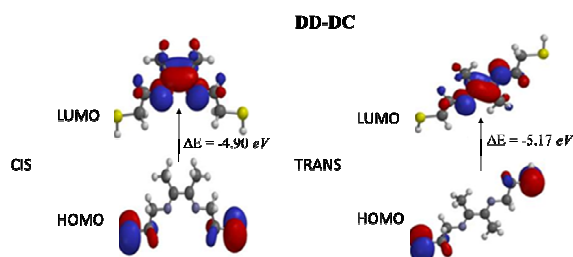


Fig. 5. Modeling of the electronic structures of the  $\alpha$ -diimine.

## Conclusions

The  $\alpha$ -diimine derivate of 2, 3-butanedione and the primary amine 2-aminoethanethiol was synthesized by two synthetic routes to give the same compound structure and they were characterized by  $^1\text{H}$  and  $^{13}\text{C}$ -NMR, EI-MS and elemental analysis. In the electrochemical studies, it is observed that the molecule DD-DC/MS acts as better corrosion inhibitor (%E= 53 at 10 ppm) than the compound obtained conventionally. The DFT analysis shows the preferential conformation for the imine, being the most stable *trans* conformation. Synthetic route affects the inhibitor properties, however a deep study of the intermolecular association or change in the molecule conformation to explain why the compound obtained by using mechanosynthesis are more efficient as corrosion inhibitor will be presented in a further theoretical study.

## Acknowledgements

To Conacyt for financial support to project (CB157534). The authors also thank to L. Velasco and Y. Marmolejo for their technical assistance.

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## Science and Materials Engineering IV

10.4028/www.scientific.net/AMR.976

## Synthesis and Mechano-synthesis of *N, N'*-bis (thylthyenil)-2,3-butanediimine with Corrosion Inhibitor Properties

10.4028/www.scientific.net/AMR.976.64

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