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Microwave-assisted Synthesis, Crystal and Molecular Structure, and DFT Study of 1-(2-aminoethyl)-2-imidazolidinethione

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Abstract. A fast microwave-assisted procedure for synthesizing 1-(2-aminoethyl)-2-imidazolidinethione (**1**) is described. The crystal and molecular structure was determined. The combination of an X-ray crystallographic study and theoretical calculations (DFT) provided insight into the understanding of the high performance of this compound as low toxicity corrosion inhibitor.

Key words: imidazolidinethione, microwave, theoretical calculations, X ray crystallography.

Resumen. Se describe un método rápido de síntesis asistida por microondas para la preparación de 1-(2-aminoetil)-2-imidazolidinethione (**1**). La combinación del estudio cristalográfico por difracción de rayos X y los cálculos teóricos (DFT) proporcionan información para entender el alto desempeño de este compuesto como inhibidor de la corrosión de baja toxicidad.

Palabras clave: Imidazolidinethione, microondas, cálculos teóricos, cristalografía de rayos X.

Introduction

The use of corrosion inhibitors is one of the most common practices for controlling the corrosion problems in chemical industries. There has been concern about the toxicity of inhibitors discharged into the environment [1], thus the development of high efficient environmental friendly corrosion inhibitors continues being an exciting topic of research.

1-(2-aminoethyl)-2-imidazolidinethione (**1**) is a well known heterocyclic compound that forms part of biologically active organic structures [2], and is highly efficient as low toxicity corrosion inhibitor for oil field applications [3].

Microwave technology has become a powerful tool in organic synthesis, since employing this technique it is generally possible to prepare organic compounds very fast, with high purity and better yields when compared to other more conventional methods [4].

It has been recently shown that theoretical calculations help to detail the understanding of some key questions about the structure-performance relationship of organic compounds that function as corrosion inhibitors [5].

As part of our research in developing new efficient corrosion inhibitors [6], and also new microwave-assisted synthetic methodologies [7], we decided to explore the structural characteristics of compound **1** from an experimental and theoretical point of view in order to develop a model and reference for comparison. This type of combined analysis may be useful for the development of new structurally related heterocycles having improved corrosion inhibitor properties.

As a result of this investigation we report herein a new, fast and efficient protocol for the microwave-promoted synthesis of **1**, completed by the X-ray structure analysis and a theoretical DFT study.

Experimental

General. Diethylenetriamine (**2**) and thiourea (**3**) were purchased from Aldrich and used as received. 2-Propanol (Aldrich) was distilled before use.

Instrumentation. Microwave irradiations were carried out utilizing a controllable single-mode MW equipment (MIC-I, 2450 MHz, max. power 600 W, from SEV, Mexico) [7].

Theoretical calculations. The calculations were performed with the Gaussian 98 program [9], using the functional hybrid B3LYP [10, 11] (Becke with three parameters for exchange and Lee, Yang, Parr for correlation functionals) and the 6-311+G** basis set for all atoms. In all cases, a full structure optimization was carried out followed by an analysis of the vibrational frequencies in order to determine whether they correspond to a minimum in the potential energy curve. The hardness [12] (η) was calculated as the half of the HOMO – LUMO gap, i.e.

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}$$

The condensed Fukui functions were calculated as [13]:

$$f_k^\alpha = \sum_{v \in k}^{AO} |C_{v\alpha}|^2 + \sum_{x \neq v}^{AO} C_{x\alpha} C_{v\alpha} S_{xv}; \alpha \equiv +, 0, -$$

where $\{C_{v\alpha}\}$ are the frontier molecular orbital coefficients and $\{S_{xv}\}$ the atomic orbital overlap matrix elements. The local softness [14] was calculated by the following equation:

$$s(\vec{r})^\alpha = Sf(\vec{r})^\alpha, \alpha = +, -, 0 \text{ and } S = \frac{1}{\eta}$$

having the above described definitions of η and f_k^α .

Synthesis. To a pyrex vessel designed for microwave synthesis (50 mL) and equipped with a stirring bar, condenser and ammonia trap, 0.010 g (0.01 mol) of diethylenetriamine and 0.060 g (0.01 mol) of thiourea were added. The mixture was irradiated under stirring with microwaves for 7 min at 100 W and a temperature of 150 ± 5 °C. The intermittent periods of cooling and mixing were 20 sec per min. The resulting product was recrystallized from 2-propanol, obtaining compound **1** (1.28 g, 88%) as light-yellow crystals.

X-ray crystallography

X-ray diffraction studies were performed on a Bruker-AXS diffractometer with a CCD area detector ($\lambda_{\text{MoK}\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 293$ K via ω/Φ -rotation at 10 s per frame (SMART) [15]. The measured intensities were reduced to F^2 and corrected for absorption with SADABS (SAINT-NT) [16]. Corrections were made for Lorentz and polarization effects. Structure solution, refinement and data output were carried out with the SHELXTL-NT program package [17, 18]. Non hydrogen atoms were refined anisotropically. C-H hydrogen atoms were placed in geometrically calculated positions using a riding model. N-H hydrogen atoms have been localized by difference Fourier maps and refined fixing the bond length to 0.86 Å; the isotropic temperature factors have been fixed to a value 1.5 times the one of the oxygen atoms. Figures were created with SHELXTL-NT. Hydrogen bonding interactions in the crystal lattice were calculated by PLATON [19].

Crystallographic data for compounds **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-272479. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Synthetic Procedures

The conventional synthesis of **1** consists in heating diethylenetriamine and thiourea at 180 °C for 5 h in an inert atmos-

phere (Scheme 1). The product in its pure form is described as a waxy solid and is obtained in a yield of 77% [2].

The literature reports several efficient, fast and simple microwave-promoted syntheses of heterocycles similar to **1**, such as benzimidazolidin-ones and -thiones [20], as well as imidazole-5-ones [21], however, a microwave-assisted synthesis of 2-imidazolidinethiones has not been described previously.

Our studies have shown that using this non-conventional energy source, compound **1** can be obtained in less than 10 min and with high purity, even in solvent-free conditions. Varying the microwave power, reaction temperature and using different solvent and solvent-free conditions, the procedure for the microwave-assisted synthesis of **1** have been optimized. The best results were obtained applying for 7 min an intermittent microwave irradiation of 100 W and at temperature of 150°C. The crude product was purified by a single recrystallization from 2-propanol, generating monocrystals suitable for a structure determination by X-ray crystallography. The molecular structure of the title compound is shown in Fig. 1.

X-ray crystallography

The most relevant crystallographic data and selected geometrical parameters for compound **1** are shown in Tables 1 and 2.

Very recently the crystal and molecular structure of a thiourea derivative was published in this journal demonstrating the importance of hydrogen bonds in this class of compounds [22]. The geometric parameters determined for **1** are

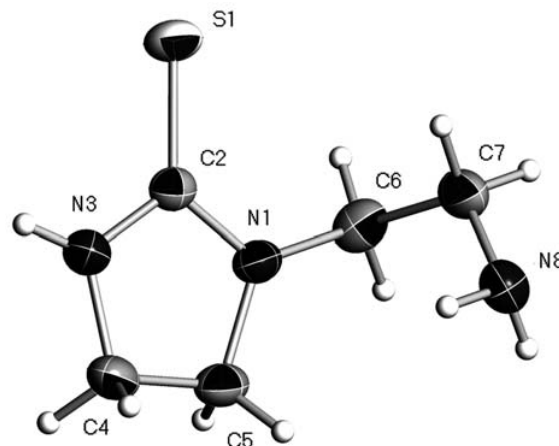
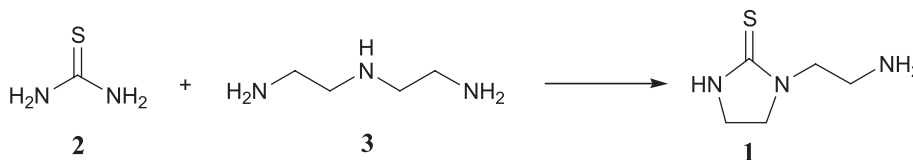


Fig. 1. Perspective view of the molecular structure of **1**.



Scheme 1. Synthesis of 1-(2-aminoethyl)-2-imidazolidinethione (**1**).

Table 1. Crystallographic data for compound **1**.

Crystal data	1
Formula	C ₅ H ₁₁ N ₃ S
Crystal size (mm ³)	0.37 × 0.43 × 0.54
MW (g mol ⁻¹)	145.23
Space group	P 2 ₁ /n
Cell parameters	
<i>a</i> (Å)	6.2913(6)
<i>b</i> (Å)	9.5671(9)
<i>c</i> (Å)	12.3553(12)
β (°)	94.607(2)
<i>V</i> (Å ³)	741.26(12)
<i>Z</i>	4
μ (mm ⁻¹)	0.354
ρ_{calcd} (g cm ⁻³)	1.30
Data collection	
θ limits (°)	2 < θ < 26
hkl limits	-7, 7; -11, 11; -15, 15
No. collected reflections	7459
No. independent reflections (<i>R</i> _{int})	1459 (0.02)
No. observed reflections ^[c]	1351
Refinement	
<i>R</i> [<i>c</i> , <i>d</i>]	0.035
<i>R</i> _w [<i>e</i> , <i>f</i>]	0.093
No. of variables	91
GOOF	1.04
$\Delta\rho_{\text{min}}$ (e Å ⁻³)	-0.16
$\Delta\rho_{\text{max}}$ (e Å ⁻³)	0.17

in well agreement with this structure and the X-ray structures of several 2-imidazolidinethiones that have been also reported [23]: C=S, 1.683(2) Å; C-N_{imid}, 1.336(2) and 1.330(2) Å. Most of the compounds studied so far present either intermolecular N'-H...N or N-H...S hydrogen bonding interactions. In the crystal lattice of compound **1** each molecule is involved in N'-H...N hydrogen bonds, thus giving crinkled 1D hydrogen bonded chains (0.86 Å, 2.01 Å, 2.86 Å, 172 °). These chains are further linked through C-H...S interactions (0.97 Å, 2.94 Å, 3.65 Å, 130 °).

Theoretical Study

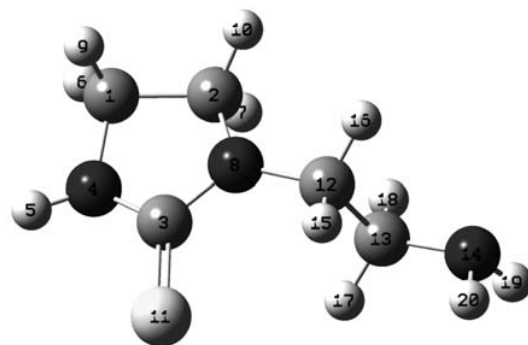
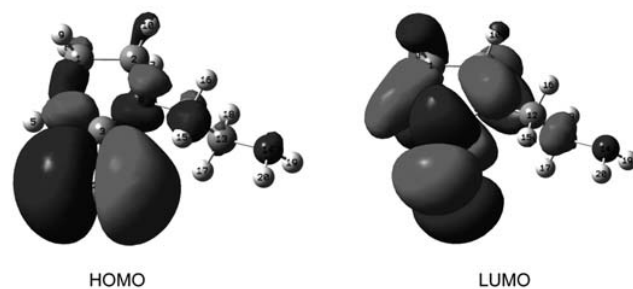
The geometry of **1** was optimized using a B3LYP hybrid functional and 6-311+G** basis set (Fig. 2) and is in good agreement with the structure obtained by the X-ray diffraction study (see Table 2). In Table 3 some additional parameters obtained from the structure optimization of **1** are presented.

Since in the ground state the frontier molecular orbitals are involved in the activity properties of corrosion inhibitors, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) have been analyzed (Fig. 3).

Table 2. Theoretically and experimentally determined bond distances, bond angles and torsion angles for compound **1**.

		Theoretical	Experimental
Bond distances (Å) ^a	S11-C3	1.675	1.683(2)
	C3-N4	1.374	1.330(2)
	C3-N8	1.365	1.336(2)
	C1-N4	1.461	1.449(2)
	C2-N8	1.464	1.463(2)
	C1-C2	1.539	1.500(3)
	N8-C12	1.453	1.447(2)
	C12-C13	1.536	1.510(3)
	C13-N14	1.465	1.454(2)
	C3-N8-C12	124.3	125.4(1)
Bond angles (°) ^a	S11-C3-N4	124.9	124.4(1)
	S11-C3-N8	127.5	126.3(1)
	C3-N4-C1	111.1	112.1(1)
	C3-N8-C2	111.1	111.1(1)
	C2-C1-N4	100.6	103.0(1)
	C1-C2-N8	101.9	103.0(1)
Torsion angles (°) ^a	S11-C3-N4-C1	166.5	177.4(1)
	S11-C3-N8-C2	174.4	174.2(1)
	S11-C3-N8-C12	10.6	4.9(2)

^a For numeration please see Figure 2.

**Fig. 2.** Calculated molecular structure of **1** (B3LYP/ 6-311+G**).**Fig. 3.** Frontier orbitals calculated for **1**.

For the HOMO it is observed that the highest electron density is located at the sulphur atom, while for the LUMO the largest contributions can be attributed to the carbon and sulfur atoms. The Fukui function for nucleophilic and electrophilic attack presented in Table 4 permitted to calculate a softness value of 0.359 (hardness, $\eta = 2.78$). The Fukui functions show clearly that the atom in the molecule that is most reactive at nucleophilic sites is carbon C3, while at electrophilic sites, such as activated metal surfaces, it is the sulphur atom. The same behavior can be deduced from the indexes of local softness. Additionally, the Fukui function shows that the sulphur atom possesses the capacity to function as electron acceptor. This allows to corroborate the inhibitory activity of this compound, since according to theory a good inhibitor should be both a good electron-donating agent and a good electron acceptor (retrodonation) in order to stabilize the electron deficiency or electron excess at active metal surfaces that are susceptible for corrosion.

The reactivity of a molecule can be also examined by an analysis of the electrostatic potential. In Fig. 4 the isosurface of the electrostatic potential is shown at a cut of 0.02. This presentation confirms the results of the Fukui function analysis, since it can be seen that the sulphur atom has the largest negative value of the electrostatic potential (red = negative, blue = positive), so that the molecule can suffer an electrophilic attack at this position. Also nitrogen atom N14 presents a negative value, but this is significantly smaller than that of the sulphur atom.

These results show that the combined analysis of the structural and electronic features of a molecule is useful for

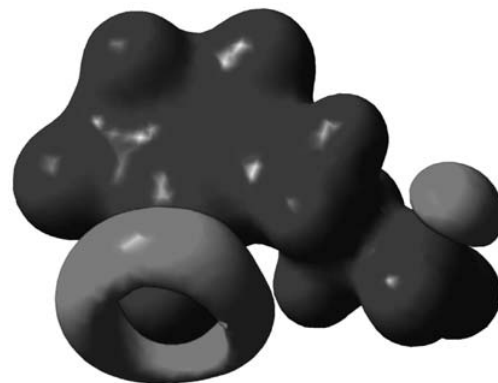


Fig. 4. Electrostatic potential of compound 1.

the understanding of the structure-performance relationship of corrosion inhibitors, thus allowing for the design of new and better heterocyclic compounds with applications.

Conclusions

A fast and easy methodology for the synthesis of 1-(2-aminoethyl)-2-imidazolidinethione was developed. The combination of an X-ray crystallographic study and theoretical calculations provided insight into the understanding of the high performance of this compound as corrosion inhibitor. The results will support future research projects focused on the search for new imidazolinethione derivatives or analogous heterocycles with applications as low toxicity corrosion inhibitors.

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Table 3. Local Indexes for all atom centers in compound **1** (Fukui function for nucleophilic (f_k^+), electrophilic (f_k^-) attack, local softness for nucleophilic (s_k^+) and electrophilic (s_k^-) attack).

Number	Atom	f_k^+	f_k^-	s_k^+	s_k^-
1	C	0.01	0.01	0.00	0.00
2	C	0.01	0.00	0.00	0.00
3	C	0.50	0.04	0.18	0.01
4	N	0.09	0.01	0.03	0.00
5	H	0.01	0.00	0.00	0.00
6	H	0.00	0.00	0.00	0.00
7	H	0.01	0.00	0.01	0.00
8	N	0.11	0.02	0.04	0.01
9	H	0.01	0.00	0.00	0.00
10	H	0.01	0.00	0.00	0.00
11	S	0.21	0.89	0.07	0.32
12	C	0.01	0.01	0.00	0.00
13	C	0.01	0.00	0.00	0.00
14	N	0.00	0.00	0.00	0.00
15	H	0.00	0.00	0.00	0.00
16	H	0.00	0.00	0.00	0.00
17	H	0.00	0.00	0.00	0.00
18	H	0.00	0.00	0.00	0.00
19	H	0.00	0.00	0.00	0.00
20	H	0.00	0.00	0.00	0.00

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