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Synthesis and Crystal Structure of 3-Amino-1-(5-Chloro-2-Hydroxyphenyl)Imidazolidine-2,4-Dione

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The present study describes the synthesis, spectral data, and single crystal X-ray structural analysis of 3-amino-1-(5-chloro-2-hydroxyphenyl)imidazolidine-2,4-dione. X-Ray analysis revealed that the title compound did not have the anticipated structure, but had that of a different substance. This unexpected conformation generated the interest in studying the synthesis of this compound. The inspected compound, 3-amino-1-(5-chloro-2-hydroxyphenyl)imidazolidine-2,4-dione, is a pharmaceutical intermediate and is nonplanar. Its benzene and five-membered rings have a dihedral angle of 53.95(7)°. The conformation is stabilized by intermolecular O—H ... O, O—H ... N, and N—H ... O interactions and a weak C—H ... π interaction.

Keywords 2,4-dione; 3-amino; structure; synthesis; X-ray

Introduction

Compounds bearing a 1,2,4-triazole moiety have been reported to have antimicrobial [1–5], antitubercular [2,5], analgesic [2,6], anti-inflammatory [6], antiviral [7,8], and cyclin-dependent kinase 5/p25 inhibitory [9] activities. In addition, many compounds, which carry a 5-chloro-2(3*H*)-benzoxazolone ring, have been reported to have diverse biological activities, including muscle relaxant [10], antimicrobial [11,12,13], analgesic, and anti-inflammatory activities [14]. Therefore, these findings prompted us to synthesize new 1,2,4-triazole derivatives attached to position 3 of the 5-chloro-2(3H)-1,3-benzoxazolone ring via a methylene bridge; however, the synthesis achieved a 3-aminoimidazolidine-2,4-dione instead of the desired 3-[(4-amino-5-thioxo-1,2,4-triazol-3-yl)methyl]-5-chloro-2(3*H*)-benzoxazolone. Milcent et al. [15] have reported the cyclic transformations of

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2(3H)-benzoxazolone derivatives into triazinones, N-(2-hydroxyphenyl)-2-oxazolidinones, imidazolin-2-ones, and imidazolidine-2,4-diones. These cyclic transformations were, in part, the result of facile ring opening of oxazolone by various nucleophiles such as primary alkyl amines and hydrazine, among others. This study aims to disclose the unexpected synthesis of 3-amino-1-(5-chloro-2-hydroxyphenyl)imidazolidine-2,4-dione, and its structural features, including X-ray analysis. The title compound and its derivatives could be different and could also have different biological activities. This would be the scope of our further studies.

Experimental

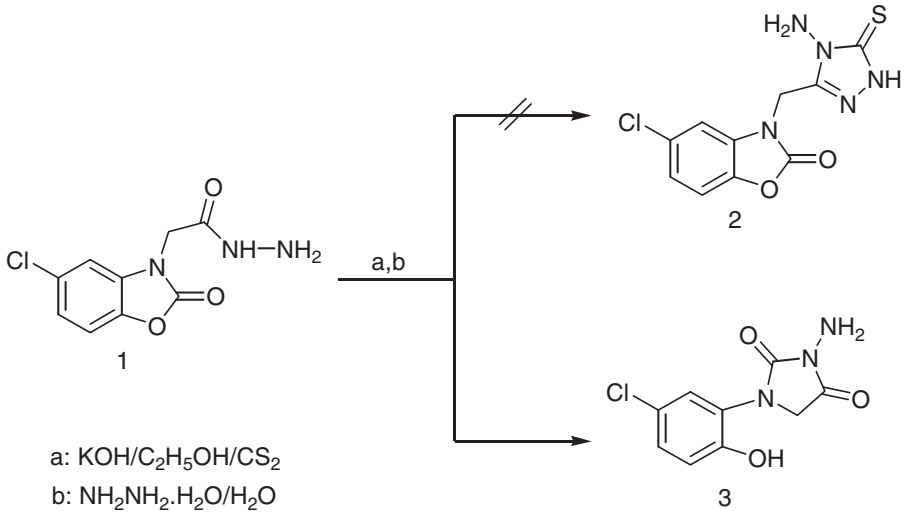
Chemicals and Instrumentation

The melting points of the compounds were determined on an Electrothermal-9200 digital melting point apparatus and are uncorrected. The IR spectra of the compounds were recorded on a Bruker Vector 22 IR spectrometer as KBr disks. The ^{1}H NMR spectra were recorded with a Varian Mercury-400 FT-NMR spectrometer (Varian Inc., Palo Alto, CA, USA) in DMSO-d_6. The mass spectra were obtained on a Waters ZQ micromass LC-MS spectrometer (Waters Corporation, Milford, MA, USA) using ESI(+) mode. Elemental analysis was performed on a Leco 932 CHNS instrument (St. Joseph, MI, USA) and the results were within $\pm$ 0.4% of the theoretical values.

Synthesis of Compound 3-Amino-1-(5-Chloro-2-Hydroxyphenyl) Imidazolidine-2,4-Dione

2-(5-chloro-2(3*H*)-benzooxazolon-3-yl)acetohydrazide was synthesized by the methods reported in the literature [10,11,16].

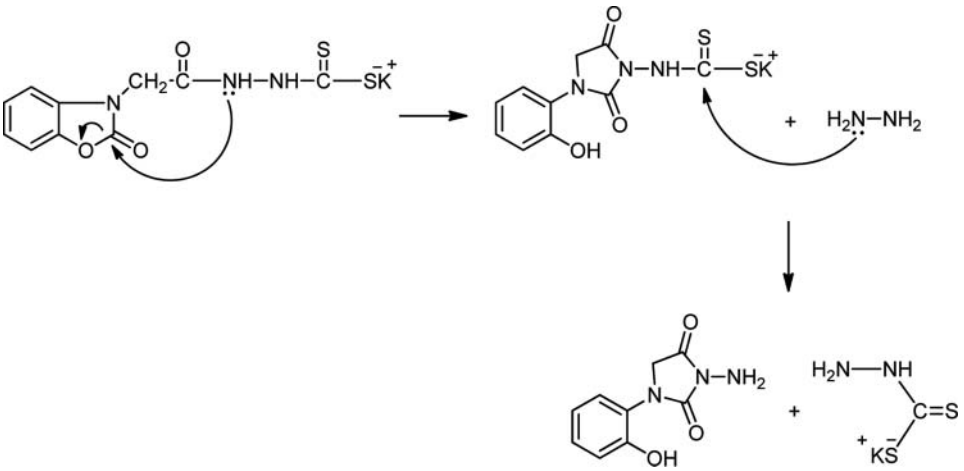
This compound (**1**) reacted with carbon disulphide in ethanolic potassium hydroxide at room temperature to give potassium dithiocarbazate, which was directly used



Scheme 1. Synthesis of compound 3.

for the next step without further purification. These carbazates reacted with excess hydrazine hydrate upon heating in water or ethanol to afford not 3-[(4-amino-5-thioxo-1,2,4-triazol-3-yl)methyl]-5-chloro-2(3*H*)-benzoxazolones (**2**), but 3-amino-1-(5-chloro-2-hydroxyphenyl)imidazolidine-2,4-dione derivative (**3**) (Scheme 1).

It was reported in the literature [15] that 2-oxo-3-benzoxazoleacetohydrazides gave imidazolidine-2,4-dione derivatives by the intramolecular nucleophilic attack of the amido group to the carbonyl group of benzoxozolone moiety. In the present case, heating of dithiocarbazate with hydrazine, a strong base, caused the similar reaction to produce imidazolidine-2,4-dione derivative **3** prior to triazole derivative **2** as shown in Scheme 2. Afterwards the reaction with the second hydrazine molecule might remove the dithiocarbazate moiety.



Scheme 2. Formation of imidazolidine ring.

The product was filtered, washed thoroughly with cold water, dried, and recrystallized from ethanol. The yield was 13% and the melting point was 247°C (ethanol) (Lit., 265°C, water) [15]. TOF MS (EI^+) calculated for $C_9H_8ClN_3O_3$: 242.0332; found: 242.0332.

Elemental analysis: $C_9H_8ClN_3O_3$, calculated (%)/found (%): C: 44.74/44.54, H: 3.34/3.32, N: 17.39/17.43.

Crystal Structure Analysis

The crystal structure of the title compound was solved by direct methods and was refined by a full-matrix least-squares method on F^2. A summary of the crystallographic data is given in Table 1.

A single crystal suitable for X-ray diffraction obtained in ethanol was colorless and prismatic. Measurements were performed at 296 K on an STOE IPDS 2 X-AREA [17] diffractometer with Mo $K\alpha$ radiation to $\theta_{max} = 27.5^\circ$. Cell parameters were obtained from 7871 reflections. The cell was refined on a STOE X-AREA and the data were reducted on a X-RED32 and corrected for absorption using integration [17]. Of 4829 measured reflections, 2197 were independent ($R_{int} = 0.023$). The structure was solved by direct methods using SIR-97 [18], and refined by a full-matrix least-squares procedure using the program SHELXL-97 [19]. All non-hydrogen atoms were refined aniostropically. The hydroxyl and amine H atoms were found in the difference Fourier maps and their positional

Table 1. The results of the X-ray structure analysis of the title compound

Crystal data	
$C_9H_8ClN_3O_3$	$D_x = 1.662$ Mg m^{-3}
$M_r = 241.63$	Mo $K\alpha$ radiation
Orthorhombic, $F2dd$	Cell parameters from 7871 reflections
$a = 6.9679$ (5) Å	$\theta = 1.5^\circ$–28.0°
$b = 20.2386$ (15) Å	$\mu = 0.39$ mm^{-1}
$c = 27.398$ (2) Å	$T = 296$ (2) K
$V = 3863.7$ (5) Å^3	Prism, colorless
$Z = 16$	0.47 × 0.42 × 0.23 mm
Data collection	
STOE IPDS 2 diffractometer	2047 reflections with $I > 2\sigma(I)$
ω scan	$R_{int} = 0.023$
Absorption correction: integration	$\theta_{max} = 27.5^\circ$
$T_{min} = 0.838$, $T_{max} = 0.916$	$h = -9 \rightarrow 9$
4829 measured reflections	$k = -26 \rightarrow 23$
2197 independent reflections	$l = -35 \rightarrow 35$
Refinement	
Refinement on F^2	Calculated weights $w = 1/[\sigma^2(F_o{}^2) + (0.0397P)^2 + 0.3089P]$, where $P = (F_o{}^2 + 2F_c{}^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.063$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$S = 1.06$	$\Delta\rho_{min} = -0.18$ e Å^{-3}
2197 reflections	Extinction correction: none
154 parameters	Absolute structure [25]: 998 Freidel pairs
Mixture of independent and constrained H-atom refinement	Flack parameter: −0.04 (5)

parameters were refined by softly restraining with the DFIX instruction (N—H = 0.85 (2) Å and 0.876 (18) Å, and O—H = 0.85 (2) Å). Their isotropic thermal parameters were treated in the riding model $U_{iso}(H) = 1.2\ U_{eq}(N)$ for amine and $1.5\ U_{eq}(O)$ for hydroxyl.

Table 2. The important IR and ^{1}H NMR signals of the title compound

IR (KBr, cm^{-1})	^{1}H NMR (DMSO-d_6, δ)
3337	10.21 (1H, s, OH)
3210	7.38 (1H, d, J = 2.8 Hz, H^6)
1770	7.23 (1H, dd, J = 2.8 Hz; 8.6 Hz, H^4)
1706	7.21 (1H, d, J = 8.6 Hz, H^3)
	4.89 (2H, s, CH_2)
	4.26 (2H, s, NH_2)

Table 3. Final coordinates and equivalent isotropic displacement parameters of non-hydrogen atoms (Å^2). $U_{eq} = (1/3)\sum i \sum jUijai^*a_j^*\left(a_i.a_j\right)$

Atom	*x*	*y*	*z*	U_{eq}
Cl1	0.67515 (6)	0.12512 (2)	0.02235 (2)	0.0484 (1)
O1	−0.02921 (15)	0.02227 (6)	0.11056 (4)	0.0452 (4)
O2	0.51338 (15)	−0.10594 (6)	0.10570 (4)	0.0407 (3)
O3	0.01477 (19)	−0.20738 (6)	0.02800 (5)	0.0491 (4)
N1	0.23167 (17)	−0.06393 (6)	0.07359 (4)	0.0303 (3)
N2	0.2835 (2)	−0.17158 (6)	0.06846 (4)	0.0336 (3)
N3	0.3841 (2)	−0.23061 (7)	0.07471 (5)	0.0412 (4)
C1	0.4416 (2)	0.02868 (7)	0.05489 (5)	0.0314 (4)
C2	0.4681 (2)	0.09638 (8)	0.05056 (5)	0.0330 (4)
C3	0.3310 (2)	0.14049 (8)	0.06651 (5)	0.0354 (4)
C4	0.1640 (2)	0.11657 (7)	0.08705 (5)	0.0357 (4)
C5	0.1314 (2)	0.04881 (7)	0.09140 (5)	0.0317 (4)
C6	0.2709 (2)	0.00502 (7)	0.07428 (5)	0.0285 (3)
C7	0.3608 (2)	−0.11188 (7)	0.08495 (5)	0.0305 (4)
C8	0.1108 (2)	−0.16368 (7)	0.04552 (5)	0.0333 (4)
C9	0.0680 (2)	−0.09083 (8)	0.04712 (5)	0.0337 (4)

The remaining H atoms were positioned geometrically and refined using a riding model with the C—H distances of 0.93 Å and 0.97 Å with $U_{iso}(H) = 1.2\ U_{eq}(C)$.

A molecular plot was prepared with ORTEP-3 for Windows [20]. The software used to prepare material for publication was WINGX with publication routines [21].

Results and Discussion

Spectral Studies

The synthesized compound was characterized by elemental analysis, IR, ^{1}H NMR, and mass spectroscopic data. The structure was unambiguously assigned by X-ray diffraction studies. The ^{1}H NMR data of the compound obtained in DMSO-d_6 solution were given in the experimental section and was consistent with the structural results. The significant absorption bands of the compound are given in Table 2. The results of elemental analysis closely correlated with calculated values within the error limits.

Description of the Crystal Structure of 3

The ORTEP of the title compound along with the atom-numbering scheme is shown in Fig. 1. Crystal data and details for the crystal structure determination of the compound are listed in Table 1. Atomic parameters are given in Table 3, and selected bond lengths, angles, and torsion angles in Table 4. The benzene ring (C1–C6) and the five-membered ring (N1/N2/C7–C9) are essentially planar and oriented with a dihedral angle of 53.95 (7)°. The Cl atom and the hydroxyl group are located in the plane of the benzene ring to which they are connected, with maximum deviations of –0.086 (1) Å for Cl1 and 0.000 (1) Å for

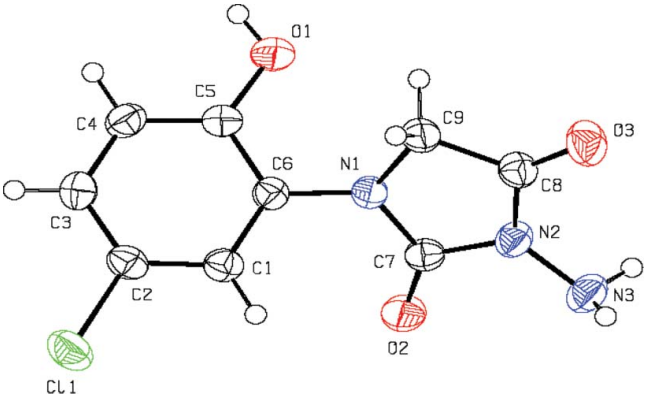


Figure 1. An ORTEP view of the title molecule with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

O1. One amino and two carbonyl groups are located in the plane of the five-membered ring, with maximum deviations of –0.033 (1) Å for O2, 0.015 (1) Å for O3, and –0.020 (1) Å for N3. A similar study [22] indicated that both rings are also located in the same plane but the possibility to form intramolecular H-bonds does not exist, and this structure is richer in energy at 27.5 kJ/mol. The C7–O2 and C8–O3 bonds were double bonds with bond lengths of 1.212 (2) Å and 1.208 (2) Å, respectively. In addition, the C5–O1 and C2–Cl1 bond lengths were 1.348 (2) Å and 1.737 (2) Å, respectively. These values were consistent with those reported previously, 1.223 (2) Å and 1.217 (2) Å [23], and 1.354 (2) Å and 1.739 (2) Å [24].

Table 4. Selected bond lengths (Å), angles (°), and torsion angles (°) of the title compound

Bond lengths	Bond angles	Torsion angles
Cl1-C2 1.737 (2)	Cl1-C2-C3 119.98 (12)	C6-N1-C9-C8 166.08 (12)
O1-C5 1.348 (2)	C6-N1-C9 121.58 (12)	C7-N1-C9-C8 2.30 (14)
O2-C7 1.212 (2)	C2-C1-C6 119.17 (13)	C6-N1-C7-O2 15.0 (2)
C2-C3 1.379 (2)	C7-N1-C9 111.42 (12)	C9-N1-C7-O2 178.16 (14)
N1-C7 1.359 (2)	O2-C7-N1 128.12 (14)	C6-N1-C7-N2 –165.69 (12)
N1-C6 1.422 (2)	C6-N1-C7 124.76 (12)	C9-N1-C7-N2 –2.52 (15)
N2-C7 1.398 (2)	O2-C7-N2 125.14 (14)	C7-N1-C6-C1 43.42 (19)
N2-C8 1.367 (2)	N3-N2-C8 126.77 (12)	C7-N2-C8-O3 179.96 (14)
N2-N3 1.396 (2)	N1-C7-N2 106.74 (12)	N3-N2-C8-C9 –178.14 (12)
N1-C9 1.457 (2)	C7-N2-C8 112.75 (12)	N3-N2-C7-O2 -0.9 (2)
C5-C6 1.397 (2)	O3-C8-C9 128.23 (13)	C8-N2-C7-O2 –178.91 (14)
C1-C6 1.388 (2)	N3-N2-C7 120.44 (13)	N3-N2-C7-N1 179.74 (12)
C4-C5 1.395 (2)	N2-C8-C9 106.00 (12)	C8-N2-C7-N1 1.75 (16)
C3-C4 1.380 (2)	N1-C6-C1 119.88 (12)	C7-N2-C8-C9 –0.29 (15)
C1-C2 1.388 (2)	C1-C6-C5 120.41 (13)	N2-C8-C9-N1 –1.16 (14)
C8-C9 1.505 (2)	Cl1-C2-C1 118.64 (11)	O3-C8-C9-N1 178.59 (15)

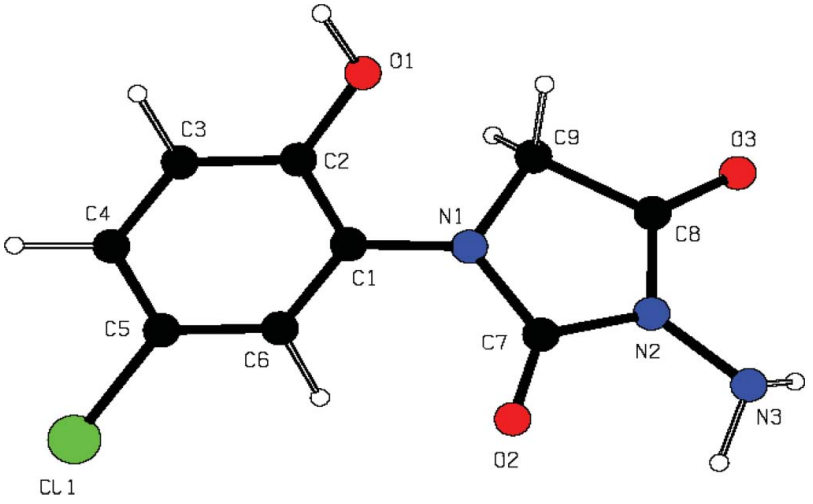


Figure 2. Spatial view of the molecular model calculated by the CNDO approximation.

Theoretical Study

Quantum mechanical calculations with the CNDO approximation were also carried out [26]. The spatial view of the single molecule considered in vacuum is shown in Fig. 2. Its dipole moment was approximately 4.33 D, and the HOMO and LUMO energy levels were −11.0827 eV and 3.7237 eV, respectively. The dihedral angle between the benzene and five-membered rings was theoretically calculated as 49.32°. This value was smaller than that of the experimental result of 53.95 (7)°.

The crystal structure is stabilized by intermolecular O−H ... O, O−H ... N, and N−H ... O interactions (Table 5). The Packing diagram of **3** is given in Fig. 3. A weak C−H ... π interaction was also observed in the structure.

Table 5. Hydrogen-bond parameters (Å, °)

	D—H	H... *A*	D... A	*D*—*H*...*A*
O1—H1... O2[a]	0.85 (2)	2.17 (2)	3.0031 (17)	166 (2)
O1—H1... N3[i]	0.85 (2)	2.44 (2)	2.9415 (18)	119.0 (17)
N3—H3A... O2[b]	0.85 (2)	2.49 (2)	3.2828 (18)	155.4 (19)
N3—H3B... O3[c]	0.876 (18)	2.340 (18)	3.2129 (19)	174.9 (18)
C4—H4... O2[a]	0.93	2.49	3.2500 (18)	139
C9—H9B... O1	0.97	2.47	2.9529 (19)	111
C9—H9A... Cg2[d]	0.97	2.88	3.6345 (15)	135

Symmetry codes: (a) −3/4 + x, 1/4 + y, 1/4 − z; (b) x, −1 + y, –1 + z; (c) −1 + x, y, −1 + z; (d) x, −y, −z.

Cg2 is a centroid of the benzene ring (C1–C6).

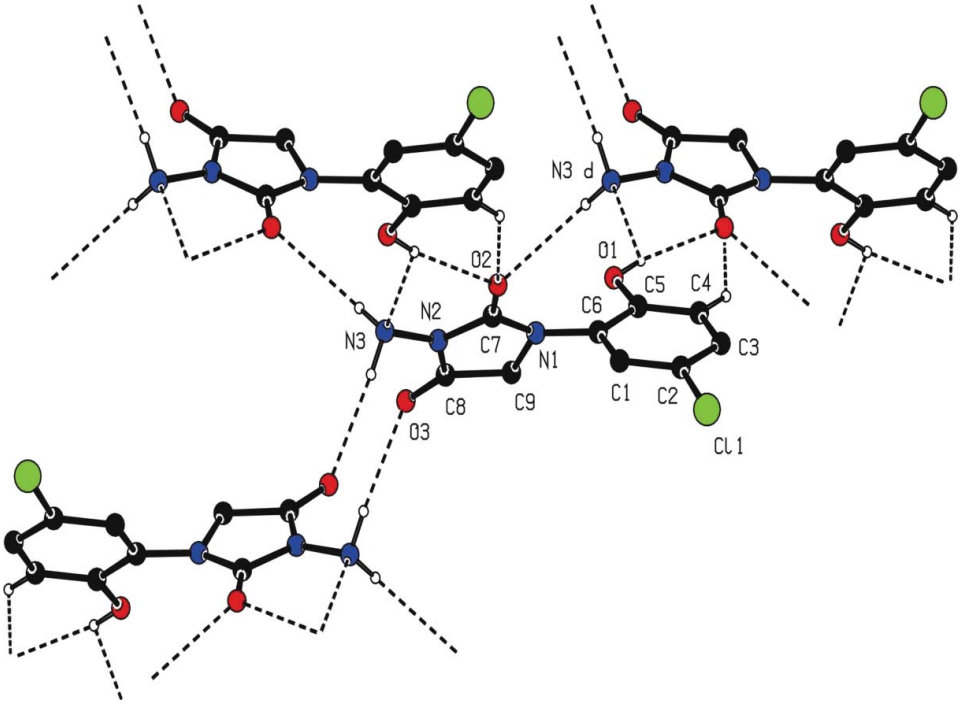


Figure 3. The hydrogen bonding interactions of the title compound viewed along the *a*-axis. H atoms not participating in the hydrogen bonding have been omitted for clarity. (Symmetry code: (d) −1/4 + x, −1/4 + y, 1/4 − z).

Conclusion

In conclusion, $C_9H_8ClN_3O_3$, 3, has been synthesized and structurally characterized. We summarize the results from synthesis and X-ray diffraction measurements for 3 single crystal. In this study, X-ray analysis revealed that the product did not have the anticipated structure, but had that of a different substance. This situation is very interesting. For this reason, we revealed the structure of the compound 3 experimentally and theoretically.

The conformation is stabilized by intermolecular O—H ... O, O—H ... N, and N—H ... O interactions and a weak C—H ... π interaction. The molecule of **3** had a nonplanar conformation. The dihedral angle between the benzene and five-membered rings was experientially calculated as 53.95(7)° and theoretically as 49.32°. According to the quantum mechanical calculations with the CNDO approximation, atoms Cl, O1, O2, and O3 have larger negative charges. The charges were calculated as −0.171, −0.257, −0.451, and −0.386 e, respectively. The total energy, binding energy, and dipole moment of molecule were −176.35 a.u., −12.23 a.u., and 4.33 debye, respectively. Biological studies on **3** are under progress and will be reported soon. Its biological significance will be discussed in detail in our further studies.

Supplementary Information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 823136 for

compound 3-amino-1-(5-chloro-2-hydroxyphenyl)imidazolidine-2,4-dione. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336–033; e-mail: deposit@ccdc.cam.ac.uk.

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