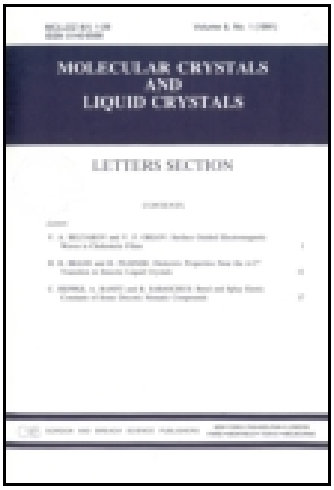

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Synthesis, Crystal Structure, and Characterization of (Z)-2-(3-chlorophenyl)-N′-hydroxyacetamidine

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Synthesis, Crystal Structure, and Characterization of *(Z)*-2-(3-chlorophenyl)-*N'*-hydroxyacetamidine

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The compound (Z)-2-(3-chlorophenyl)-N'-hydroxyacetamidine, (2) was synthesized and characterized by ^{1}H NMR, FT-IR, TGA, UV-Visible Spectra, and elemental analysis. Its molecular structure was solved by single-crystal X-ray diffraction method. The title molecule, $C_8H_9ClN_2O$ is crystallized in the monoclinic crystal system with the space group $P2_1/c$ and with unit cell parameters $a = 8.7092(4)$ Å, $b = 8.2370(4)$ Å, $c = 12.5256(6)$ Å, $\beta = 102.252(3)^\circ$, and $Z = 4$. The molecular and crystal structure of the title molecule is stabilized by an intramolecular interaction of the type N—H···O, and the intermolecular interactions of types N—H···N and O—H···N.

Keywords Amidoxime; characterization; crystal structure; molecular interactions

Versatile heterocyclic compounds were generally synthesized from carbonitrile. The reaction of carbonitrile with hydroxylamine hydrochloride gave amidoximes. Amidoximes are compounds bearing both a hydroxyimino and an amino group at the same carbon atom which makes them versatile building blocks for the synthesis of various heterocycles [1]. 1,2,4-oxadiazole skeleton are pharmacologically active and constructed mainly based on the coupling reaction of amidoximes with carbonyl compounds using various coupling agents [2]. The importance of amidoximes in chemistry along with their rich biology, make them an attractive target for medicinal chemists, biochemists, and biologists. Their numerous pharmaceutical applications such as bactericidal and fungicidal [3], local anesthetics [4], antitumor and antimalarial agents [5], and their ability to release NO were clarified, giving a new insight to their mode of action and allowing the design of novel therapeutic agents. Motivated by these reflections, it was contemplated to synthesize the title compound (*Z*)-2-(3-chlorophenyl)-*N'*-hydroxyacetamidine which is well characterized by the single-crystal X-ray diffraction, ^{1}H NMR, FT-IR, thermogravimetric analysis (TGA), UV-Visible Spectra, and elemental analysis.

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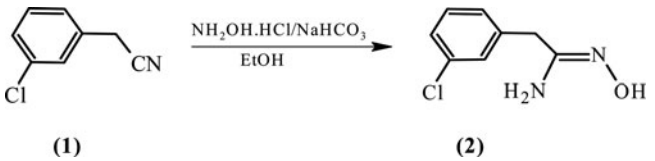
2. Experimental

2.1. Materials and Methods

Melting point was taken in an open capillary tube and was uncorrected. The purity of the compound was confirmed by thin-layer chromatography using Merck silica gel 60 F_{254} coated aluminum plates. IR spectrum was recorded on Shimadzu-FTIR Infrared spectrometer in KBr (ν_{max} in cm^{-1}). ^1H NMR (400 MHz) spectrum was recorded on a Bruker Avance II 400 spectrometer, with 5 mm PABBO BB-1H TUBES, using $CDCl_3$ as a solvent and TMS as internal standard (chemical shift in δ ppm). A TA-SQT Q600 thermogravimetric analyzer was used to obtain the TGA curve under nitrogen atmosphere with a heating rate of 10°C min^{-1}. The UV-Vis spectrum was recorded on a Shimadzu UV-2550 UV-Visible spectrophotometer. Elemental analysis was carried out by using VARIO EL-III (Elementar Analysensysteme GmBH).



Scheme 1. Synthesis of Compound (*Z*)-2-(3-chlorophenyl)-*N'*-hydroxyacetamidine.

2.2. Procedure for the Preparation of (Z)-2-(3-chlorophenyl)-N'-hydroxyacetamidine (2)

Sodium bicarbonate (70 mmol, 5.88 g) was added in portions to a solution of hydroxylamine hydrochloride (70 mmol, 4.79 g) in 15 ml of water. A solution of (3-Chlorophenyl) acetonitrile (35 mmol, 4.14 ml) in 40 ml of ethanol was then added, and the mixture stirred under reflux for 6 h. The precipitate formed was filtered off and recrystallized from ethanol. Yield 82%, m.p. 108–110°C.

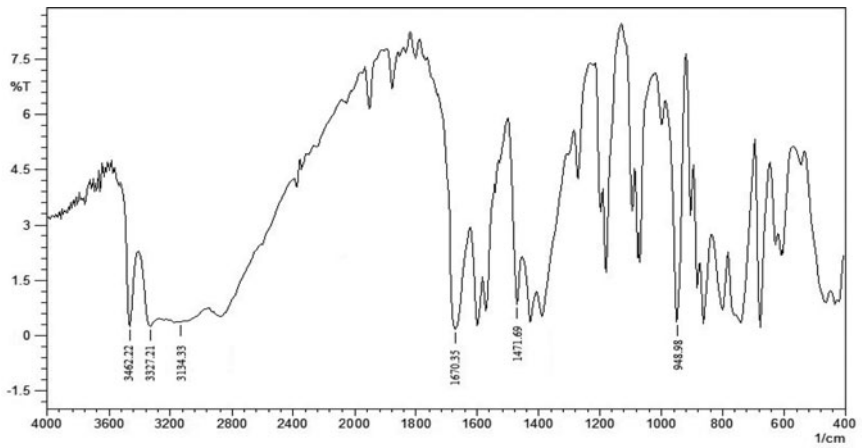


Figure 1. FT-IR spectrum.

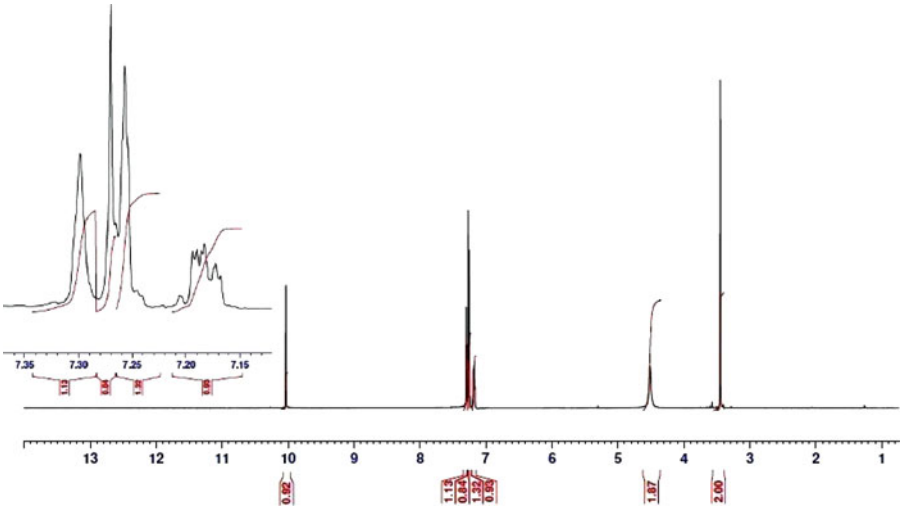


Figure 2. ^{1}H NMR spectra.

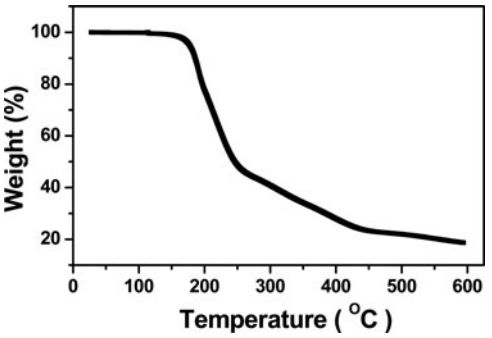


Figure 3. TGA thermogram of compound.

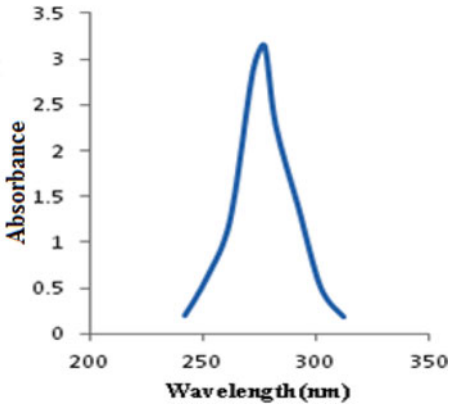


Figure 4. UV-Visible spectrum.

Table 1. Elemental analysis for $C_8H_9ClN_2O$

Element	Experimental (%)	Calculated (%)
Carbon	52.08	52.04
Nitrogen	15.13	15.17
Hydrogen	4.95	4.91

3. Results and Discussion

3.1. FT-IR Spectral Analysis

The FT-IR spectrum of the crystal structure was shown in Fig. 1. IR spectra showed strong absorption bands at 3327 and 3462 cm^{-1} due to primary amine group and vibration band at 3134 cm^{-1} due to the hydroxyl group. The absorption peak at 1670 cm^{-1} is due to the stretching vibration that corresponds to −C=N group. The C−H deformation vibration in CH_2 is observed at 1471 cm^{-1}. The absorption at 948 cm^{-1} is characteristic of N-O stretching vibration in amidoxime moiety.

3.2. ^{1}H NMR Spectral Analysis

The ^{1}H NMR spectrum of the crystal structure was shown in Fig. 2. ^{1}H NMR spectrum showed sharp singlet at δ 3.45, 4.50 and δ 10.10 ppm due to CH_2, NH_2, and OH protons, respectively. The four aromatic protons resonated as a multiplet in the region of δ 7.17–7.32 ppm.

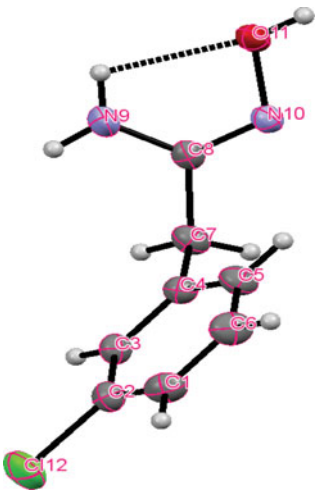


Figure 5. *ORTEP* view of the title molecule with atom numbering scheme. Displacement ellipsoids for nonhydrogen atoms are drawn at 30% probability level. Dashed line indicates intramolecular hydrogen bond of the type N−H···O.

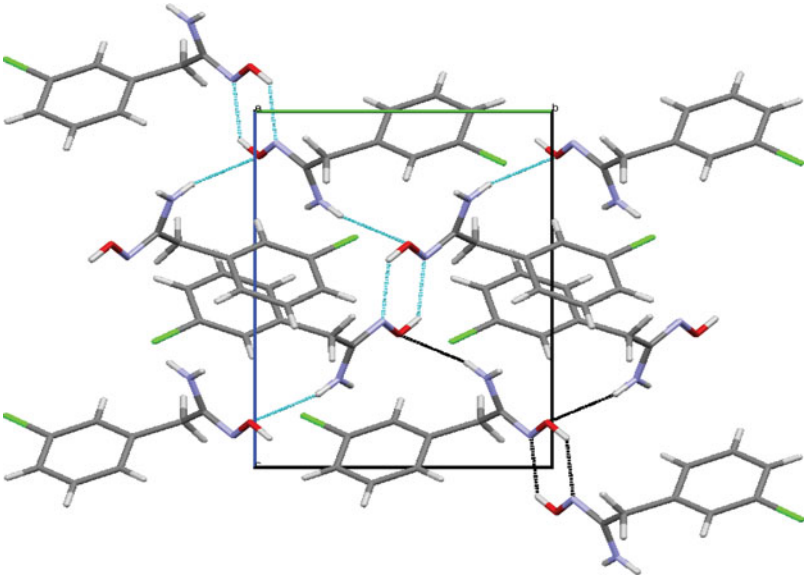


Figure 6. Packing of molecules when viewed down *a*-axis.

3.3. Thermogravimetric Analysis (TGA)

The TG analysis thermogram (solid line) of the compound is shown in Fig. 3. TGA of compound **2** has been performed in the temperature range 30°C–600°C at a rate of 10°C min^{-1} under N_2 atmosphere. The TGA curve shows that compound 2 exhibits a remarkable thermal stability at about 150°C. The compound decomposes mainly into two stages on heating between the room temperature and 470°C. The following decomposition pattern suggested explains the TGA. The first weight loss is 49.0% in the range of 150°C–250°C, which is ascribed to the loss of hydroxycyanamide and chlorine atom (calculated 50.0%). These results show that amidoxime bonds are weaker than parent nitrile bonds. With further heating, the 28.0% of the compound (calculated 29.4%) decomposed between 250°C and 470°C, which is ascribed to the passing of an acetylene molecule. The differences between the experimental and calculated weight losses in both stages of decomposition are small and are within the experimental errors. Above 470°C, 23% of the residue were left out which is due to the charring of carbon. Hence, the TG study confirms the formation of the compound in the stoichiometric ratio.

3.4. UV-Vis Spectral Analysis

Like FT-IR spectroscopy, UV spectroscopy is also useful in the evaluation of the compounds. On UV, electronic spectrum compounds are analyzed based on the characteristic frequencies corresponding to definite groups and it is shown in Fig. 4. The UV-Vis spectrum was recorded by using methanol as a solvent. From the graph, it was observed that the compound shows an absorption peak at 275 nm. The transmittance of the compound is due to the π–π^* transition of the constituent group. Hence, the material may be useful for optoelectronic applications.

Table 2. Crystal data and structure refinement

Parameter	Value
CCDC deposit No.	945517
Empirical formula	$C_8H_9ClN_2O$
Formula weight	184.62
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 8.7092(4)$ Å $b = 8.2370(4)$ Å $\beta = 102.252(3)$ $c = 12.5256(6)$ Å
Volume	878.09(7) Å^3
Z, Calculated density	4, 1.397 Mg/m^3
Absorption coefficient	3.469 mm^{-1}
$F_{(000)}$	384
Crystal size	0.23 × 0.20 × 0.19 mm
Theta range for data collection	5.2 to 64.4°
Limiting indices	$-10 \leq h \leq 9$, $-9 \leq k \leq 7$, $-14 \leq l \leq 11$
Reflections collected / unique	5474 / 1442 [R(int) = 0.042]
Completeness to theta = 64.4°	97.8%
Max. and min. transmission	0.559 and 0.503
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1442/0/110
Goodness-of-fit on F^2	1.07
Final R indices [I>2sigma(I)]	$R1 = 0.0541$, $wR2 = 0.1467$
R indices (all data)	$R1 = 0.0584$, $wR2 = 0.1520$
Extinction coefficient	0.0095(19)
Largest diff. peak and hole	0.30 and –0.44 e. Å^{-3}

3.5. Elemental Analysis

In order to confirm the chemical composition of the synthesized compound, Carbon (C), Hydrogen (H), and Nitrogen (N) analysis was carried out. The experimental and calculated percentages of C, H, and N are given in Table 1. The differences between experimental

Table 3. Selected bond lengths and angles (Å,°)

Cl(12)–C(2)	1.745(3)
O(11)–N(10)	1.446(2)
N(10)–C(8)	1.285(3)
N(9)–C(8)	1.343(3)
C(8)–N(10)–O(11)	110.19(19)
N(10)–C(8)–N(9)	125.1(2)
N(10)–C(8)–C(7)	116.4(2)
N(9)–C(8)–C(7)	118.5(2)
C(1)–C(2)–Cl(12)	119.14(19)
C(3)–C(2)–Cl(12)	119.10(19)

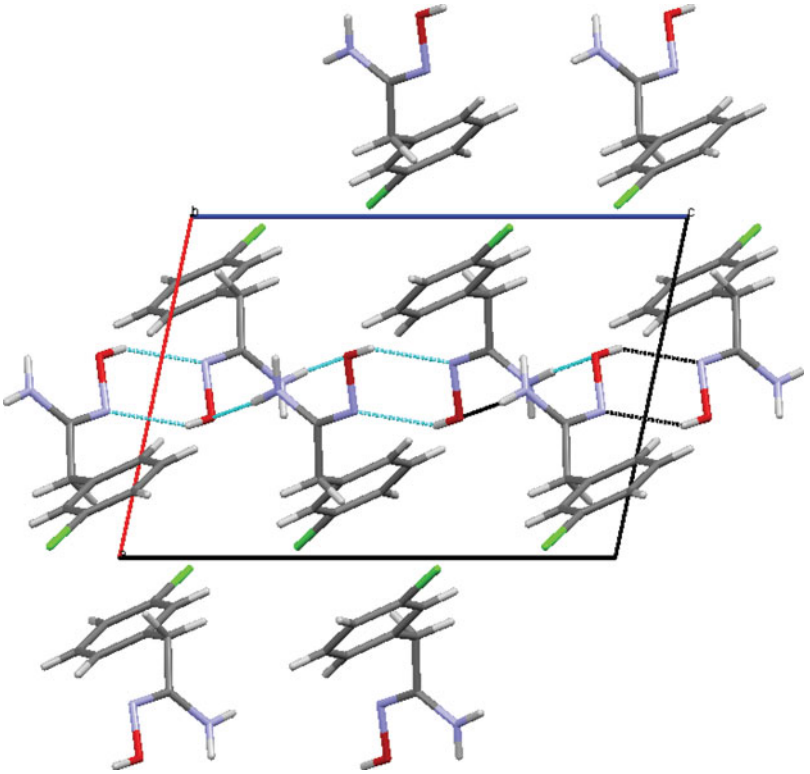


Figure 7. Packing of molecules when viewed down *b*-axis.

Table 4. Selected torsion angles (°)

N(10)–C(8)–C(7)–C(4)	102.9(3)
N(9)–C(8)–C(7)–C(4)	−78.6(3)
C(3)–C(4)–C(7)–C(8)	129.2(2)
C(5)–C(4)–C(7)–C(8)	−53.9(3)
O(11)–N(10)–C(8)–C(7)	179.71(19)
O(11)–N(10)–C(8)–N(9)	1.2(3)

Table 5. Hydrogen bond geometry (Å, °)

D—H···A	d(D—H)	d(H···A)	d(D···A)	<(DHA)
N9—H9*A*···O11*	0.86	2.26	2.570(3)	101
N9—H9*B*···O11$_{(i)}$	0.86	2.21	3.039(3)	162
O11—H1···N10$_{(ii)}$	0.82	2.11	2.766(3)	137

Symmetry codes: (i) 1−*x*, −1/2+y, 1/2−*z*; (ii) 1−*x*, 2−*y*, 1−*z*.
*Intramolecular interaction.

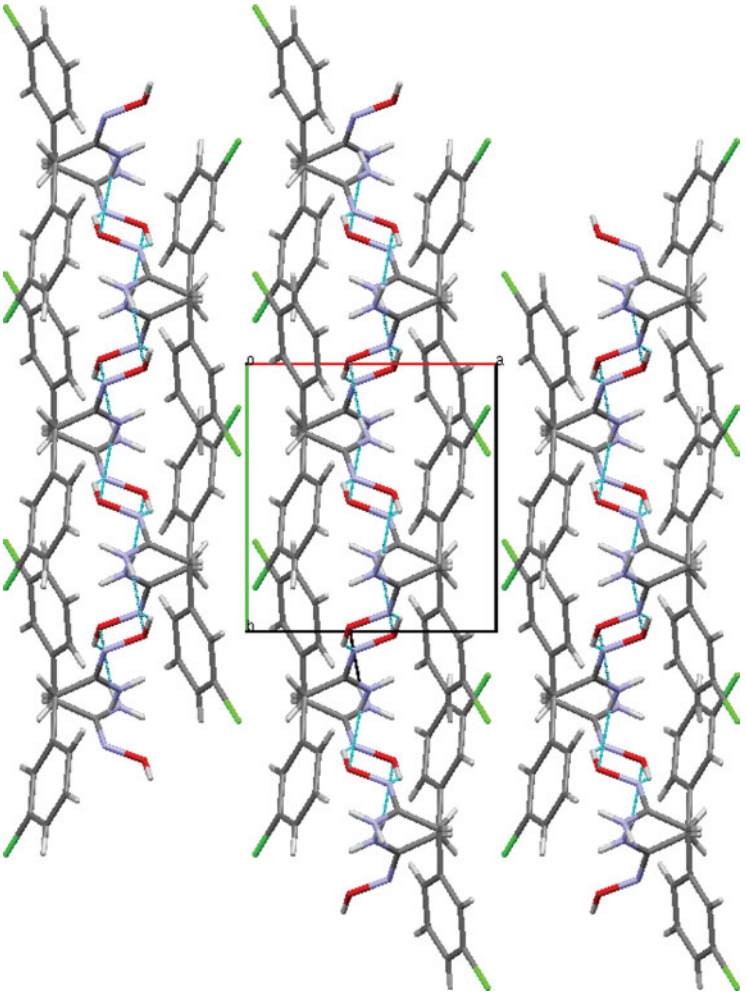


Figure 8. Packing of molecules when viewed down *c*-axis.

and calculated percentages of C, H, and N were very close to each other and within the experimental errors. This confirms the formation of the product in the stoichiometric proportion.

3.6. Single Crystal X-Ray Diffraction Method

A colorless block-shaped single crystal of size 0.23 × 0.20 × 0.19 mm of the title compound was selected for data collection. X-ray intensity data were collected for the title compound at temperature 296 K, on Bruker AXS Proteum2 CCD diffractometer with X-ray generator operating at 45 kV and 10 mA, using CuK_α radiation of wavelength 1.54178 Å. Data were collected for 24 frames per set with different settings of ϕ (0° and 90°), keeping the scan width of 0.5°, exposure time of 5 s, the sample to detector distance of 45.10 mm, and 2θ value at 46.6° [6]. A complete dataset is processed using the software *SAINT PLUS* [7]. The structure was solved by direct methods and refined by full-matrix least squares method

on F^2 using *SHELXS* and *SHELXL* programs [8]. All nonhydrogen atoms were revealed in the first difference Fourier map itself. All hydrogen atoms were positioned geometrically (C–H = 0.93 Å, N–H = 0.86 Å, O–H = 0.82 Å) and refined using a riding model with $U_{iso}(H) = 1.2\ U_{eq}$ (C,N) and $U_{iso}(H) = 1.5\ U_{eq}$ (O). After several cycles of refinement, the final difference Fourier map showed peaks of no chemical significance and the residual is saturated to 0.0541. The geometrical calculations were carried out using the program *PLATON* [9]. The molecular and packing diagrams were generated using the software *MERCURY* [10].

X-ray diffraction analysis revealed that the title compound is crystallized in the monoclinic crystal system with the space group $P2_1/c$. The unit cell parameters are $a = 8.7092(4)$ Å, $b = 8.2370(4)$ Å, $c = 12.5256(6)$ Å, $\beta = 102.252(3)^\circ$ and $V = 878.09(7)$ Å^3. The *ORTEP* view of the title molecule with displacement ellipsoids drawn at 30% probability level is shown in Fig. 5.

The packing of molecules when viewed down *a*-axis, *b*-axis, and *c*-axis are as given in Fig. 6, Fig. 7, and Fig. 8, respectively. The crystal data and structure refinement details are given in Table 2. Bond lengths and bond angles are given in Table 3. Torsion angles are given in Table 4. Hydrogen-bond geometry is given in Table 5.

Torsional angles of 179.71(19)° about O11—N10—C8—C7 and 1.2(3)° about O11—N10—C8—N9 confirm that C7 atom and the amidoxime chain are planar. The chlorine-substituted phenyl ring, C1/C2/C3/C4/C5/C6 lies in the equatorial position with respect to the plane described by the chain C7—C8—N9—N10—O11 containing amidxoime, confirmed by the dihedral angle 76.83(12)°. The overall geometry is similar to the molecule 4-Chlorobenzamidoxime [11].

An intramolecular interaction N9–H9A···O11 forms a five membered planar ring C8/N9/H9A/O11/N10 with amidoxime chain. The crystal structure exhibits N9–H9A···π interaction (N9–H9A···$C_g(1)$ [where $C_g(1)$ is the centroid of the ring C1/C2/C3/C4/C5/C6 with a symmetry code 1–*x*,1/2+*y*, 1/2–*z*] with a N—C_g distance of 3.484(3) Å, N—H···C_g angle of 139°) and the structure is stabilized by the intermolecular hydrogen bond interactions of types N—H···O and O—H···N, giving two-dimensional chains along *bc-plane* in the crystal lattice.

4. Conclusion

The compound (*Z*)-2-(3-chlorophenyl)-*N'*-hydroxyacetamidine, (2) was synthesized and characterized by means of ^{1}H NMR, FT-IR, TGA and UV–visible spectroscopy data. The molecular structure of this compound was determined by single crystal XRD method. The crystal structure of the title compound reveals a potentially tautomeric amidoximes to be the amino-oxime form and it adopts a nonplanar *cis-syn* configuration. Spectral data show that the material may be useful for optoelectronic applications.

Acknowledgments

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