

Research Article

Synthesis, Crystal Structure and Thermal Stability of the Schiff Base N,N'-bis(2,4-dichlorobenzylidene-3-propylammonium) Amine Chloride

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Abstract

New Schiff base compound N,N'-bis(2,4-dichlorobenzylidene-3-propylammonium)amine chloride obtained by a condensation reaction between 3,3'-iminidipropylamine ($C_6H_{17}N_3$) and 2,4-dichlorobenzaldehyde ($C_7H_4Cl_2O$) in 1:2 ratio in methanol. The compound is characterized by elemental analyze (CHN) and FT-IR (Fourier-transform infrared) spectroscopic technique which shows the presence of the imine group resulting from a condensation reaction and two potentiel donor sites. Crystal structure was obtained by single-crystal X-ray diffraction (RX). Compound crystallize in the orthorhombic system, space groupe Pnma with unit cell parameters: $a = 7.0681(2) \text{ \AA}$, $b = 29.7679(10) \text{ \AA}$, $c = 11.4545(4) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 2410.06(14) \text{ \AA}^3$ and $Z = 4$. Due to a mirror plane through the molecule, the asymmetric unit consists of only half the molecule. In the crystal structure of the compound, the dihedral angle formed between an aromatic ring C08/C06/C07/C10/C13/C09 and the aliphatic group C11/C15/C14/N04/C14/C15/C11 is equal to 77.42° . In addition, the aromatic rings are in the Trans position with the aliphatic group compared to the imine bonds C12-N05 and the angle formed around C12 is $120.78(11)^\circ$ whose is sufficient to maintain the cycles in Trans configuration. Thermogravimetric analysis (TG) of the compound shows very good thermal stability and decomposition from 180°C .

Keywords

Schiff Base, Crystal Structure, 3,3'-Iminidipropylamine, 2,4-Dichlorobenzaldehyde, Spectroscopic Technique, X-Ray Diffraction, Thermogravimetric Analysis

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1. Introduction

Compounds containing an azomethine or imine group ($>C=N-$) are known as "Schiff base" in honor of Hugo Schiff (1834-1915) who first synthesized these types of compounds in 1864 [1].

They are formed by the condensation of a primary amine ($R-NH_2$) and a carbonyl compound as shown in the following reaction mechanism (Figure 1).

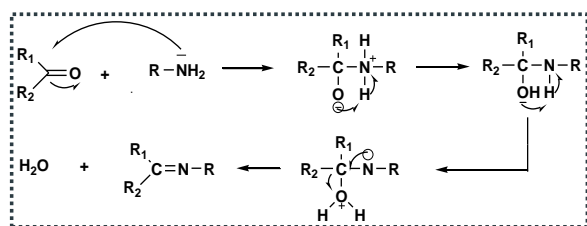


Figure 1. Schiff base formation reaction mechanism.

The first step in this reaction consists of a nucleophilic attack of the non-bonding doublet of the nitrogen atom of the amine on the carbon of the carbonyl group, leading to an unstable intermediate in which one carbon atom carries two electro attracting functions namely the hydroxyl function and the amine function. Finally, when the hydroxyl group is eliminated, the imine function $>C=N$ is immediately formed and the Schiff base is then obtained [2].

Many factors can affect the condensation reaction such as the pH of the solution, the steric effect and electronic effects [3]. In an acidic environment, the amine is rapidly protonated, so that it can no longer function as a nucleophile agent and the reaction cannot take place. Furthermore, in a strongly basic medium, the reaction is prevented due to the absence of protons in the reaction medium which causes the attack of the carbinolamine hydroxyl leading to the formation of the Schiff base and water [4].

Azomethin compounds involving aryl groups are more stable, while compounds having alkyl groups are comparatively unstable and disintegrate easily [5]. Compounds characterized by aromatic aldehydes are more stable and effective than aliphatic aldehydes [6].

Schiff bases have recently attracted attention in various fields of research, including biological activities such as antibacterial activity [7], cytotoxic activity [8], antifungal activity [9], antituberculosis activity [10], antidiabetic activity [11], anti-inflammatory activity [12], anti-Alzheimer activity [10].

2. Materials and Methods

2.1. Material and Physical Measurements

All chemicals used were of analytical grade, commercially available from different sources and used without further purification. Elemental analyses was performed on Perkin

Elmer 2400 CHN. Infrared spectra were obtained on a FTIR (Fourier-transform infrared) Spectrum Two of Perkin Elmer spectrophotometer in the $4000-400\text{ cm}^{-1}$ range. The ^1H NMR spectra in CDCl_3 was recorded at room temperature with a Bruker 200 MHz spectrometer. Thermal gravimetric (TG) analysis was conducted on a TGA SHIMADZU model 50 thermal gravimetric analyzer.

2.2. X-ray Data Collection, Structure Determination and Refinement

Reflections were measured on a Bruker D8 Quest Apex3 diffractometer with graphite monochromator Moka radiation ($\lambda = 0.71073\text{\AA}$). Software package used for the intensity integration was SAINT (v8.40A) [13] and absorption correction was performed with SADABS [14]. The structure were solved with direct methods using SHELXT-2014/5. Least-squares refinement was performed with SHELXL-2018/3 [15] against $[F_o]^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were placed on calculated positions or located in difference Fourier maps. All calculated hydrogen atoms were refined with a riding model [16]. The structures obtain were draw by the application Olex2 [17]. Crystal data and details of structure refinement for the compound are summarized in Table 1.

2.3. Synthesis of the Schiff Base

To a solution of 2,4-dichlorobenzaldehyde ($\text{C}_7\text{H}_4\text{Cl}_2\text{O}$) (3.500 g; 20 mmol) in 15 mL of methanol was added a methanolic solution (15mL) of 3,3'-iminodipropylamine ($\text{C}_6\text{H}_{17}\text{N}_3$) (1.312 g; 10 mmol) and two drops of hydrochloric acid. The reaction mixture was refluxed at for 2 h. The solution obtained is left at room temperature under slow evaporation for 72 hours. White single crystals were collected.

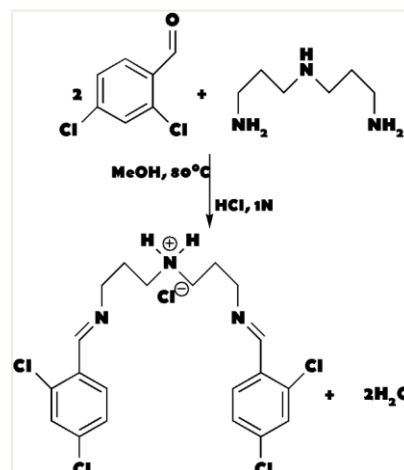


Figure 2. Synthesis scheme of the compound.

[C₂₀H₂₂N₃Cl₅]. Yield 76%. Analysis calculated, C: 47,17; H: 4,95; N: 8,67. Found, C: 47,87; H: 4,60; N: 8,72%.

3. Results and Discussion

3.1. FTIR Spectrum

The IR spectrum of the compound (Figure 3) shows the presence of vibration bands in the range 3500-2700 cm⁻¹ attributed to the ammonium cation [18, 19].

The band at 1644.63 cm⁻¹ is assigned to the $\nu_{(C=N)}$ vibration, indicates the formation of the Schiff base. The valence vibrations $\nu_{(C=C)}$ of aromatic rings are observed in the region 1600-1450 cm⁻¹. The weak band observed around 1340 cm⁻¹ is due to the valence vibration $\nu_{(C-N)}$. The hydrocarbon part is highlighted by the presence of asymmetric and symmetrical frequencies of aromatic C-H and aliphatic C-H observed respectively around 3100-3000 cm⁻¹ and 3000-2900 cm⁻¹ [19].

3.2. Thermal Analysis

TG curve of the compound was obtained at a heating rate of 5 °C min⁻¹ over a temperature range of 20-800 °C.

The TG curve of the compound (Figure 4) shows that it is thermally stable up to approximately 180 °C. The compound decomposed in two steps during the conversion. The first step was observed in the range 180 °C - 460 °C with a weight loss of 71% (calculated 71.80%) which assigned to partial elimination of two identical fragments of the ligand (2C₇H₄NCl₂) followed by a second step of the decomposition which is completed at 560 °C, implying a mass loss of 29% (calculated 28.10%) corresponded to removal of C₆H₁₄NCl fragment. The residual is zero, which confirms the total loss of the Schiff base.

3.3. Crystal Structure

The compound consists of a cationic Schiff base with a chloride ion as counter ion. The compound is symmetrical bidentate and crystallizes in an orthorhombic system with a space group Pnma and a number of units per cell Z = 4. Due to a mirror plane through the molecule, the asymmetric unit consists of only half the molecule. Disordered solvent was removed using the SQUEEZE procedure [20].

The molecular geometry is illustrated in Figure 5 and selected bond lengths and angles are listed in Table 1 are agreed with those observed in other related structure [21].

In the molecule, the aromatic rings are oriented at a dihedral angle of around 77.42°. The C12 and C15 atoms are in the Trans position relative to the N05-C11 bond.

The aromatic rings C08/C06/C07/C10/C13/C09 are in the Trans position with the aliphatic group C11/C15/C14/N04/C14/C15/C11 relative to the C12-N05 bond and the angle formed around C12 is 120.78 (11)°. This angle is sufficient to maintain the cycles in Trans configuration. The length of the C12-N05 bond is of the order of 1.2631(16) Å, which corresponds to an imine double bond (>C=N) and is to comparable to that observed for 2-((2-chloro-4-nitrophenyl)iminomethyl) phenol 1,292 (3) [22].

Furthermore, along the \vec{c} axis, the crystal structure reveals the existence of two polymeric chains formed by an alternating Schiff base ions and chloride ions. Chloride ions play an important role in crystal cohesion through the hydrogen bonds they form between Schiff base molecules (Figure 6).

In addition, there are π - π interactions [centroid – centroid distance is 3.806 Å] between adjacent aromatic rings, generating chains of molecules in the [010] direction (Figure 7). Figure 8 shows the crystal stacking seen along the \vec{a} axis.

Table 1. Crystal data and structure refinement for compound.

Formula	C ₂₀ H ₂₂ Cl ₅ N ₃
Mr	481.65
Temperature (K)	150
Crystal system, Space group	Orthorhombic, Pnma
a, b, c (Å)	7.0681(2), 29.7679(10), 11.4545(4)
Crystal size (mm)	0.43 x 0.33 x 0.10
$\alpha = \beta = \gamma$ (°)	90
V(Å ³)	2410.06 (14)
Z	4
Crystal size (mm)	0.43 x 0.33 x 0.10
Dcalc. (mg/m ³)	1.327
Absorption correction μ/mm^{-1}	0.61

F(000)	999
Θ full (°)	2.7 – 28.8
Index ranges h, k, l	$-8 \leq h \leq 10$, $-45 \leq k \leq 45$, $-17 \leq l \leq 17$
Reflections collected	46076
Independent reflections R(int)	4661 [$R_{\text{int}} = 0.022$]
Parameters	134
Indices finaux R [$I \geq 2\sigma(I)$]	$R_1 = 0.038$ $W R_2 = 0.101$
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ / e Å ⁻³	0.47/ -0.29

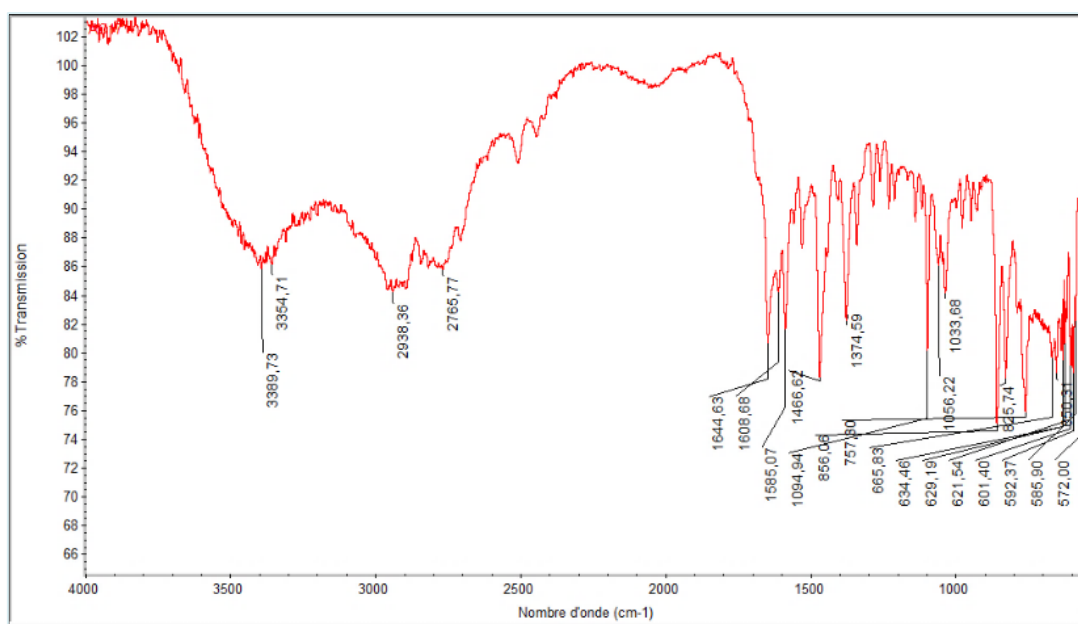


Figure 3. FT-IR Spectrum.

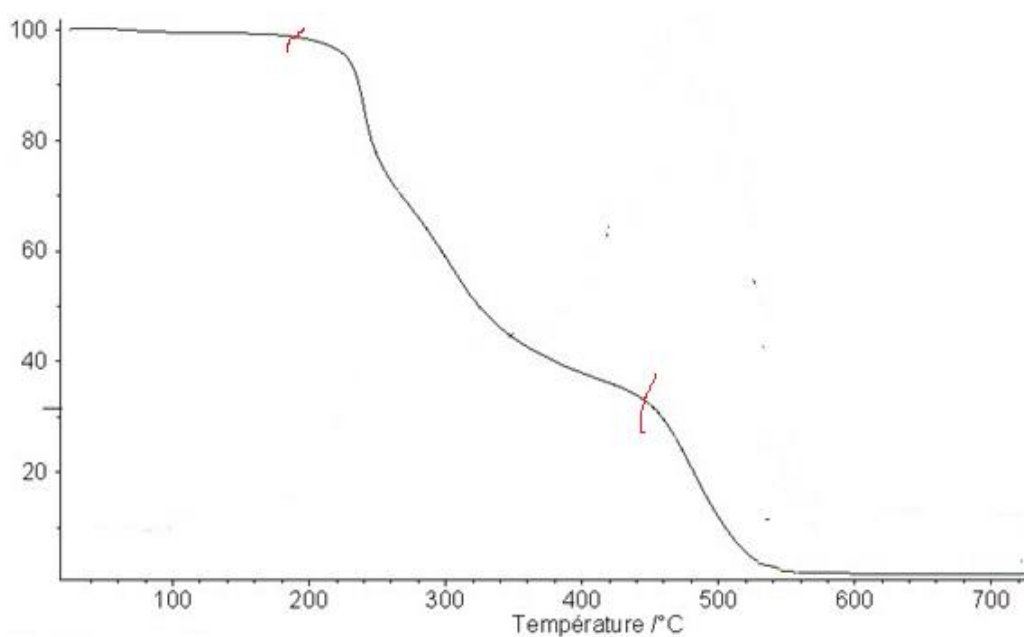


Figure 4. TG curve of the compound.

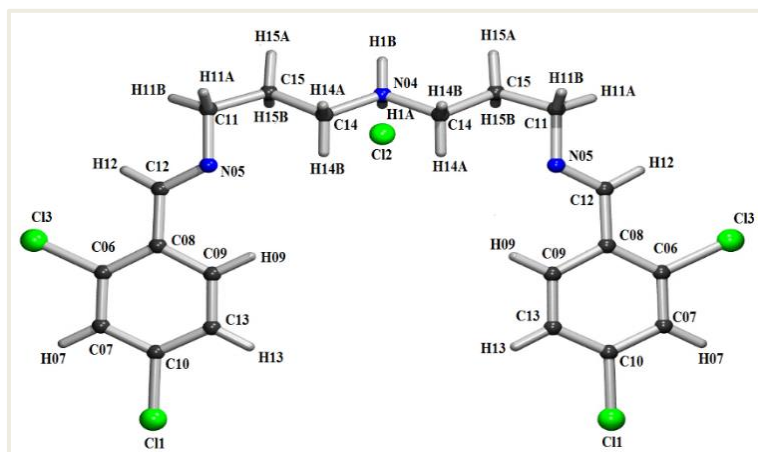


Figure 5. Crystal structure of the compound.

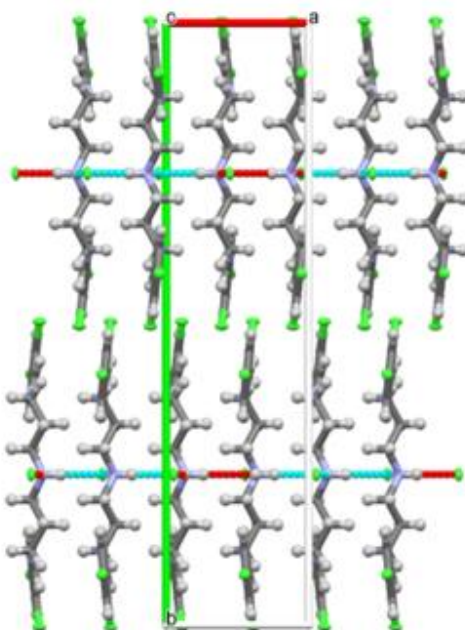


Figure 6. Crystal packing of the compound seen along the c axis. C-H...Cl hydrogen bonds are shown in blue and red lines.

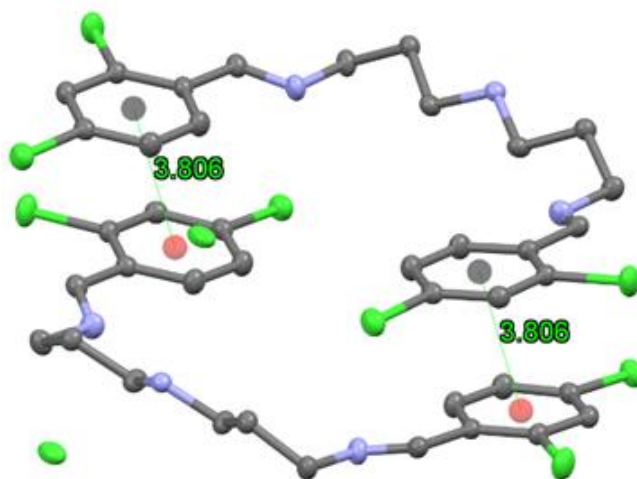


Figure 7. A molecule pair showing the centroid – centroid distance of aromatic rings between two adjacent molecules in the crystal packing.

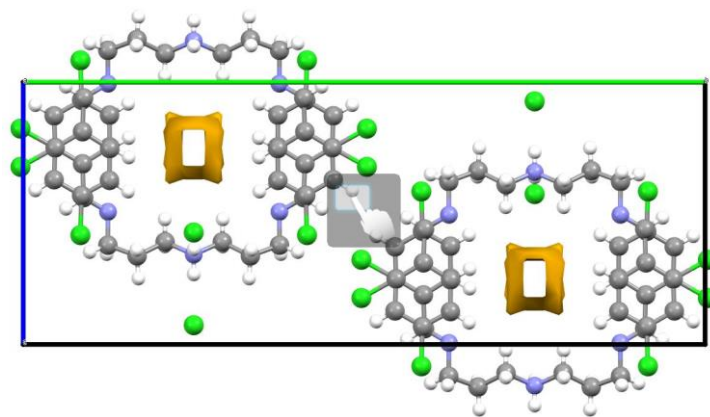


Figure 8. Crystal packig of the compound along the \vec{a} axis.

4. Conclusions

Schiff base compound N,N'-bis(2,4-dichlorobenzylidene-3-propylammonium) amine chloride, was successfully synthesized by the condensation reaction of 3,3'-iminodipropylamine and 2,4-dichlorobenzaldehyde. The structure of the compound was characterized by elemental analyses (CHN), FT-IR and X-ray diffraction which revealed a thermally stable compound, formed of a symmetrical and bidentate Schiff base ion with a chloride ion as counter ion.

Abbreviations

FTIR	Fourier-Transform Infrared
TG	Thermogravimetric
IMM	Institute for Molecules and Materials

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Supporting Information

CCDC-2376054 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Author Contributions

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original draft, Writing – review & editing

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Mouhamadou Sembene Boye: Supervision, Validation, Visualization

Dame Seye: Supervision, Validation, Visualization

Paul Tinnemans: Data curation, Formal Analysis, Resources, Software, Validation

Cheikh Abdoul Khadir Diop: Supervision, Validation, Visualization

Conflicts of Interest

The authors declare no conflicts of interest.

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