

Research Article

Synthesis, Crystal Structure, and Comparative Study of a New Organic Material 3,4-Diaminobenzophenone Semihydrate

Tarek Ben Rhaïem, Habib Boughzala, and Ahmed Driss

Laboratoire de Matériaux et Cristallographie, Faculté des Sciences de Tunis, Université de Tunis El Manar, 2092 Tunis, Tunisia

Correspondence should be addressed to Habib Boughzala; habib.boughzala@ipein.rnu.tn

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The new organic 3,4-diaminobenzophenone semihydrate (34ABPH) is grown by slow evaporation method. The compound crystallizes in the monoclinic space group: $C2$. The unit cell dimensions are $a = 28.703$ (8) Å, $b = 4.722$ (2) Å, $c = 8.7076$ (10) Å, and $\beta = 99.40$ (2)° with $Z = 2$. The crystal structure analysis reveals that the $C_{13}H_{12}N_2O$ molecules chains are organized into a double ribbon in the (b,c) plane. The structural components interact by $N-H \cdots O$ and $O-H \cdots O$ hydrogen bonds, building up a two-dimensional network. The presence of functional groups in the molecular structure is confirmed by the Fourier transform infrared (FT-IR) spectroscopy. Thermogravimetric analysis (TGA) confirms the presence of the water molecule.

1. Introduction

During the crystallization process it is common that one or more solvent molecules are involved in the structure leading to pseudopolymorphic forms. Sometimes a single molecule can give up to 15 forms between polymorphic and pseudopolymorphic. These different forms are generated by the crystallization conditions (solvent, temperature...). This crystallization phenomenon is very important in the pharmaceutical industry because it directly affects the bioavailability of drugs. In our work we have synthesized and analyzed a new pseudopolymorphic in the diaminobenzophenones family. To go deeper in molecular polymorphism many papers can be found in the literature [1, 2].

The diamine compounds are important in biological active natural products [3–5] and in medicinal chemistry [6, 7]. They are also used as auxiliaries and chiral ligands in asymmetric catalysis [8]. In this work, a new member of this family, $2C_{13}H_{12}N_2O \cdot H_2O$, is presented. Water is a highly versatile component at the interface of organic molecule. In fact, it can act both as a hydrogen bond donor and acceptor. Compared to other solvent molecules it imposes few steric constraints. It is able to establish hydrogen bond networks, occupying less space than the hydrophilic side chains of a protein. Therefore, we performed a brief comparative study

between our compound and a similar anhydrous to show the role of the water molecule in the crystal cohesion.

2. Experimental

2.1. Synthesis of (34ABPH). The crystals of the compound were prepared by slow evaporation at room temperature by mixing 3,4-diaminobenzophenone $C_{13}H_{12}N_2O$ (0.47 mmol) with a solution of manganese dibromide $MnBr_2$ (0.23 mmol) in a mixture of ethanol and water (3:1 v/v). Few weeks later, yellow crystals were obtained.

2.2. Investigation Techniques. The title compound was studied by various physicochemical methods: X-ray diffraction, DSC, TGA, and IR spectroscopy.

2.3. X-Ray Diffraction. A single crystal was selected using a polarizing microscope in order to perform X-ray diffraction analysis. Reflections intensities data were collected on an Enraf-Nonius CAD4 diffractometer [9] using graphite monochromated $MoK\alpha$ radiation, $\lambda = 0.71073$ Å.

2.4. Computing Details. Program used to solve the structure is *SHELXS97* [10], program used to refine the structure is *SHELXL97* [10], structures projections were drawn with the

TABLE 1: Crystal data of $2C_{13}H_{12}N_2O \cdot H_2O$.

Empirical formula	$2C_{13}H_{12}N_2O \cdot H_2O$
Formula weight ($\text{g} \cdot \text{mol}^{-1}$)	442.51
Crystal system	Monoclinic
Space group	C2
a	28.703 (8) Å
b	4.722 (2) Å
c	8.7076 (10) Å
β	99.40 (2)°
Z	2
Volume	1164.3 (6) Å ³
ρ_{cal}	1.262 $\text{g} \cdot \text{cm}^{-3}$
$F(000)$	468
μ MoK α	0.084 mm^{-1}
Crystal size	$0.24 \times 0.16 \times 0.12$ mm
Measured reflections	1748
Independent reflections	1687
R_{int}	0.0129
Refined parameters	202
$R[F^2 > 2\sigma(F^2)]$	0.050
$wR(F^2)$	0.132
Goodness of fit	1.16

DIAMOND program version 3.0 [11]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

2.5. Physical Measurements. The Fourier transform infrared (FT-IR) technique was carried out to confirm the presence of functional groups and to find their vibrational modes. The sample was mixed thoroughly with dried KBr. The spectrum was recorded in the range of 400 to 4000 cm^{-1} using a Bruker Vector 22 FT-IR spectrometer. The TG curve was recorded on a balance UGINE EYRAUD type B 60. DSC from SETARAM instrumentations can provide further information about phase changes and reactions occurring at elevated temperatures.

3. Results and Discussion

3.1. Crystal Structure. In accordance with the single crystal X-ray study, the title compound crystallizes as a monohydrate (Figure 1). The molecule is twisted with a dihedral angle of 54.1 (2)° between the 3,4-diaminophenyl and phenyl rings. Bond lengths and angles in the phenyl cycle are within the normal ranges and comparable with those found in homologous diaminobenzophenone [12]. Due to the 2-fold axis passing through the H_2O position in the [010] direction, the asymmetric part of the unit cell consists of a $C_{13}H_{12}N_2O$ molecule and a half water molecule. The nitrogen atoms of the amine groups are in a trigonal pyramidal configuration (sum of valence angles is 354.1° for N1 and 328° for N2) and deviate from phenyl plane, respectively, by -0.076 (4) Å and 0.0041 (2) Å. Conjugation between the nitrogen unshared electron pair and the π system of the phenyl fragment leads to a shortening

TABLE 2: Hydrogen bond geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
N1-H1B...O1 ⁱ	0.96 (4)	2.10 (4)	2.956 (4)	148 (3)
O2-H11...O1	0.91 (4)	2.03 (4)	2.884 (3)	153 (5)
N1-H1A...N2	0.88 (3)	2.43 (3)	2.772 (5)	104 (1)
N1-H1A...N2 ⁱⁱ	0.88 (3)	2.25 (3)	3.100 (5)	163 (3)
N2-H2A...O2 ⁱⁱⁱ	0.91 (4)	2.28 (4)	3.162 (3)	163 (4)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, y, -z - 1$; (iii) $x, y + 1, z$.

of the N1-C11 bond (1.384 (3) Å) and N2-C12 bond (1.402 (4) Å) relatively to the standard length of a purely single N-Csp² bond (1.43–1.45 Å) [13, 14]. On the other hand, the C1-C2 bond (1.480 (4) Å) is longer than its neighbour C1-C8 (1.476 (4) Å). This is probably due to the electron delocalisation at the C8 side of the molecule (Figure 1).

The crystal structure analysis reveals that the $C_{13}H_{12}N_2O$ molecules chains are organized into a double ribbon in the (b, c) plane. These planes are connected in pairs by intermolecular hydrogen bonds O2-H11...O1 and N1-H1A...N2ⁱⁱ (symmetry code: (ii) $-x, y, -z - 1$) (see Figure 2 and Table 2).

Each water molecule is surrounded by four organic molecules $C_{13}H_{12}N_2O$ and linked to the carboxyl group and the amine radical (Figure 3). The sequence of the organic entities $C_{13}H_{12}N_2O$ and the water molecules is provided by hydrogen bonds N-H...O and O-H...O. A two-dimensional network ensures the cohesion and the structure stability.

Before making any structural comparison it is necessary to standardize the networks of the two structures. Simply make a change in the mark of the second orthorhombic structure $C_{13}H_{12}N_2O$ (4,4'-diaminobenzophenone [12]).

Compared to the anhydrous form (4,4'-diaminobenzophenone [12]), the title compound structure exhibits several common properties (cell parameters range, absence of centrosymmetry, and structural arrangement). On the other hand, the addition of two water molecules per unit cell increases the volume cell of about 80 Å³. 40 Å³ would be the volume occupied by a single water molecule in this type of structural arrangement. Furthermore, the water molecule seems to be lowering the crystal symmetry and enhancing the crystal cohesion by increasing the hydrogen bonds density.

The alignment of the water molecules along (a) and (c) axes induces their expansion compared to those of the anhydrous structure { a : 24.306 (2) to 28.703 (8) Å (18%)} and { b : 8.1110 (7) to 8.7076 (10) Å (7%)}. The title compound b parameter narrowing is probably due to the molecules closeness in the network further to the presence of the hydrogen bonds around the water molecule (Table 3).

To learn more about the water role in the structure and as published earlier [15], the anhydrous 3,4-diaminobenzophenone exhibits powerful properties in the analysis of oligonucleotides by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. It will be interesting to know if the semihydrated form (the title compound) will have comparable behavior or not. Similar work is planned.

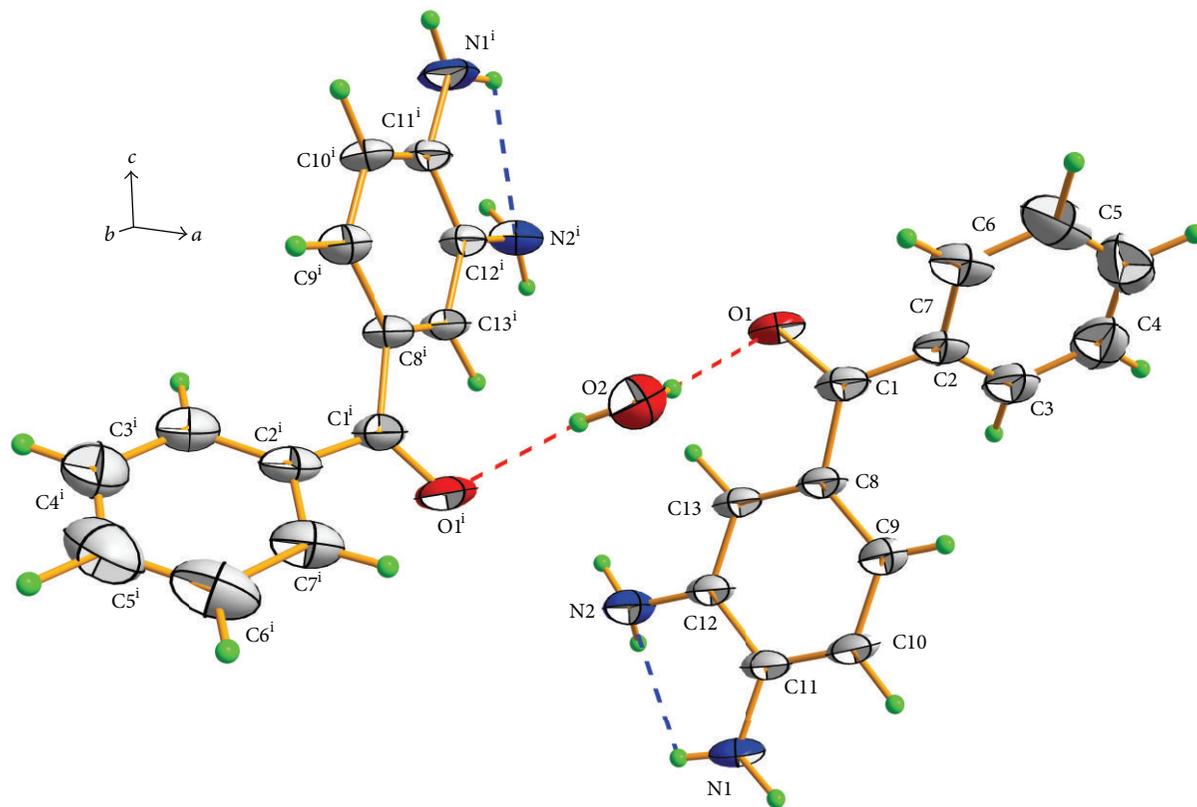


FIGURE 1: The molecular structure of the title compound, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii. Symmetry code: (i) $-x, y, -z$.

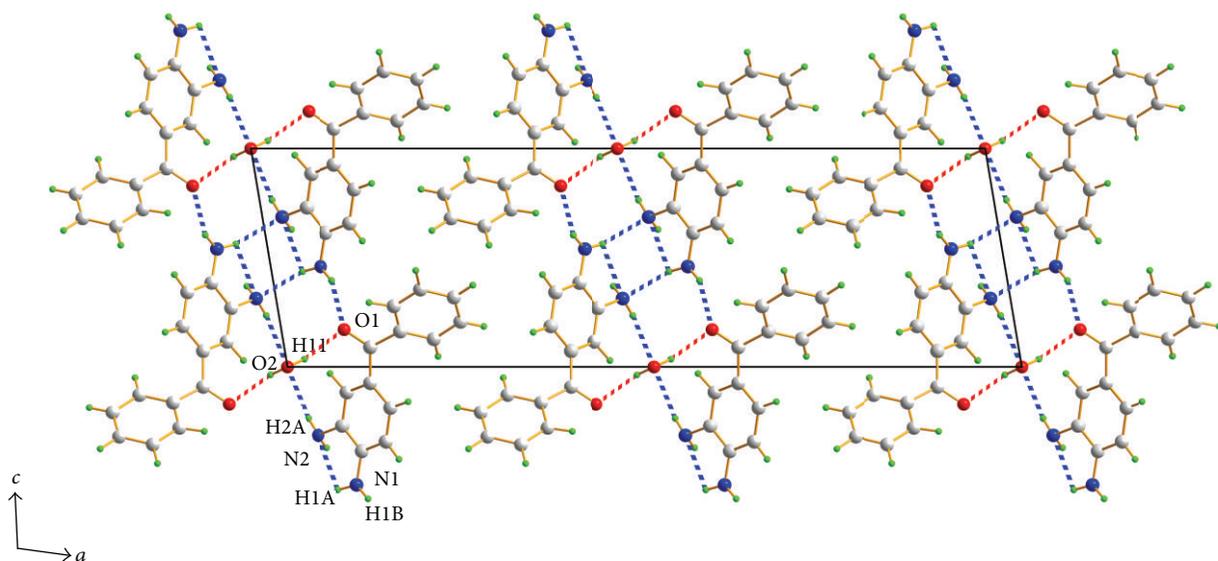


FIGURE 2: The crystal packing of the title compound, viewed along the b -axis showing the $N-H \cdots N/O$ and $O-H \cdots O$ interaction (dotted lines).

3.2. IR Spectroscopy. The infrared (IR) spectroscopy is one of the major physical methods for investigating molecular structure. Figure 4 shows the recorded IR spectrum of the title compound.

Based on the previous literature results and the theoretical simulation of IR spectrum, the large band centred around 3600 cm^{-1} is attributed to the stretching modes of $O-H$ radicals. The bands located at 3380 cm^{-1} and 3190 cm^{-1} might

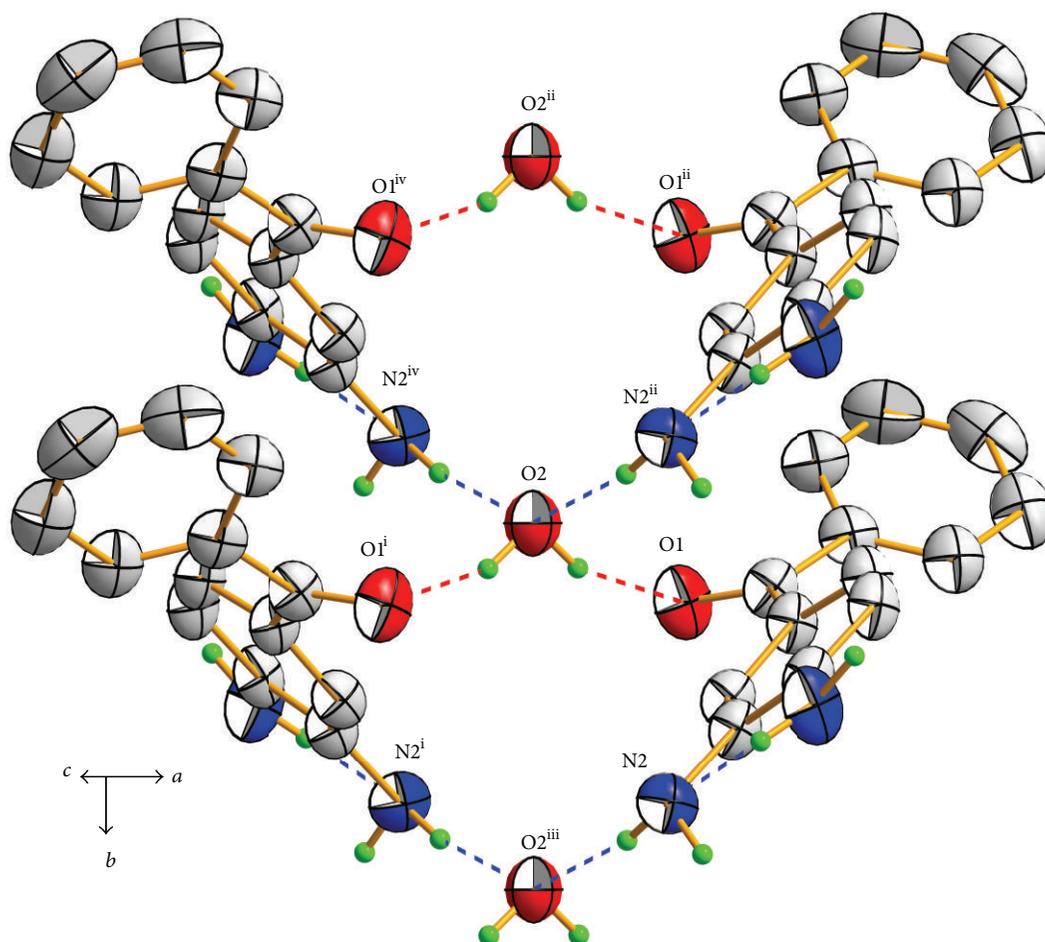


FIGURE 3: The role of water in the packing stabilization. H atoms not involved in hydrogen bonding (dashed lines) have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability level. Symmetry codes: (i) $-x, y, -z$; (ii) $x, y - 1, z$; (iii) $x, y + 1, z$; (iv) $-x, y - 1, -z$.

TABLE 3: The crystallographic parameters of $C_{13}H_{12}N_2O$ and $2C_{13}H_{12}N_2O \cdot H_2O$.

Compound	$C_{13}H_{12}N_2O$	$C_{13}H_{12}N_2O$	$2C_{13}H_{12}N_2O \cdot H_2O$
Space group	$P 2_1 2_1 2_1$	$P 2_1 2_1 2_1$	$C 2$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
a (Å)	5,4982 (5)	24,306 (2)	28,703 (8)
b (Å)	8,1110 (7)	5,4982 (5)	4,722 (2)
c (Å)	24,306 (2)	8,1110 (7)	8,7076 (10)
α (°)	90	90	90
β (°)	90	90	99,40 (2)
γ (°)	90	90	90
V (Å ³)	1083,95 (16)	1083,95 (16)	1164,3 (6)
Z	4	4	2

be assigned to the asymmetric and symmetric stretching modes of N–H in the amine group, and the out-of-plane bending mode of this group is probably responsible for the

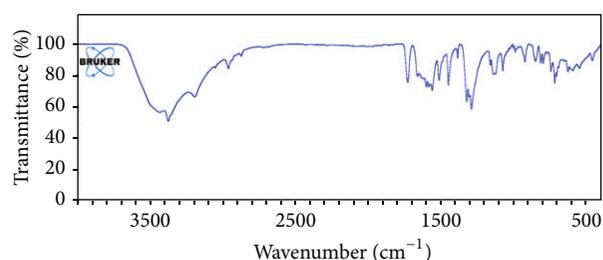


FIGURE 4: Experimental IR spectrum of compound $2C_{13}H_{12}N_2O \cdot H_2O$.

band at 1447 cm^{-1} . The bands centred at 3000 cm^{-1} could be attributed to the stretching vibration of the =C–H bonds in the aromatic group. The typical stretching band of carboxyl group ($>C=O$) is shown at 1728 cm^{-1} . However, the range of bands between 1550 and 1700 cm^{-1} is attributed to the stretching vibration of the aromatic group (C=C). Finally, the bands between 500 and 1150 cm^{-1} are probably the result of the bending vibration of the (=C–H) and (NH₂) groups.

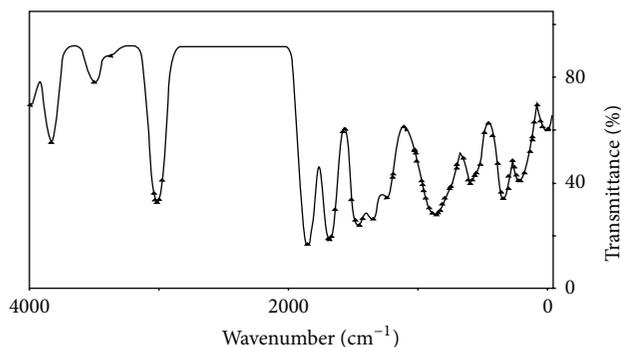
FIGURE 5: Calculated IR spectrum of compound $2C_{13}H_{12}N_2O \cdot H_2O$.

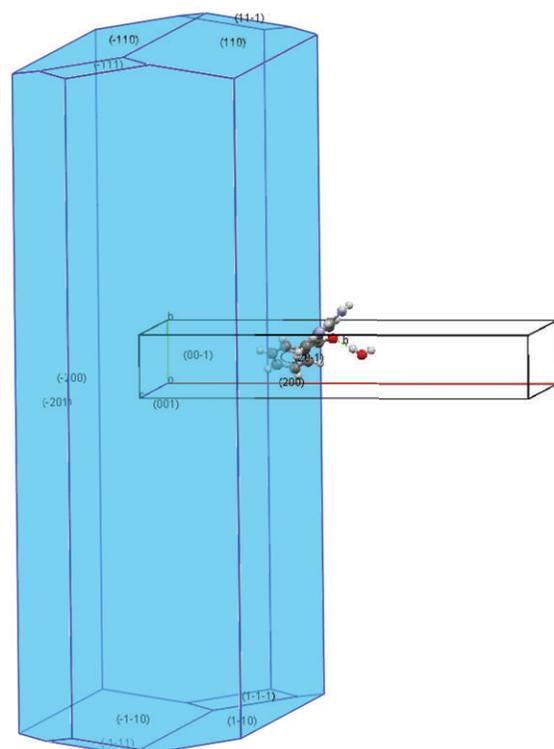
TABLE 4: Calculated and experimental IR bands.

Calculated frequencies (cm^{-1})	Experimental frequencies (cm^{-1})	Attribution
3991		
3862	3600	Stretching (O-H)
3520	3380	
3392	3190	Stretching (N-H)
3058	3000	Stretching (C-H)
1945	1728	Stretching (C=O)
1790	1550–1700	Stretching (C=C)
1748	1512	Bending (O-H)
1688	1447	Bending (N-H)
1242–1628	1200–1330	Stretching (C=C), (C-N)
500–1150	500–1150	Bending (C-H), (N-H)

3.3. Theoretical IR Spectroscopy. The semiempirical parameterized model number 3 (PM3) treatment used by “CACHe” [16] program allows the IR vibrational frequencies calculations. On the other hand, the observed bands assignment becomes easier by comparing the observed frequencies and those calculated. Figure 5 shows the IR calculated spectrum after an optimisation of the molecular configuration. This model is very close to the obtained one by the structural investigations. The main observed vibrational bands are identified in the calculated one (see Table 4).

3.4. Morphology of (34ABPH). The crystal morphology is a key element in many industrial processes and has an enormous impact at the processing and postprocessing stages of pharmaceuticals, agrochemicals, petrochemicals, and cements. The morphology of crystalline solids influences their physical properties. Crystal morphology can alter the dissolution rate of chemicals and bioavailability of drugs and mechanical properties such as filtration, grinding, dusting and handling, and packaging and storage of crystalline products.

The Bravais-Friedel-Donnay-Harker (BFDH) laws [17, 18] are strictly based on the symmetry of the crystal lattice to generate an ordered list of possible growing faces. The view of the observed and calculated crystal morphologies reveals a

FIGURE 6: Predicted morphology of $2C_{13}H_{12}N_2O \cdot H_2O$. Growth shape from BFDH rules.FIGURE 7: Images of the growth morphologies of $2C_{13}H_{12}N_2O \cdot H_2O$.

similarity between the two shapes (see Figures 6 and 7). This examination is used to assign the crystal growth axis as the (001) and to identify the crystallographic axis and the physical ones.

3.5. Thermal and Calorimetric Analysis. Calorimetric and thermal studies were carried out to investigate the thermal behaviour of the studied phase. Both techniques were used

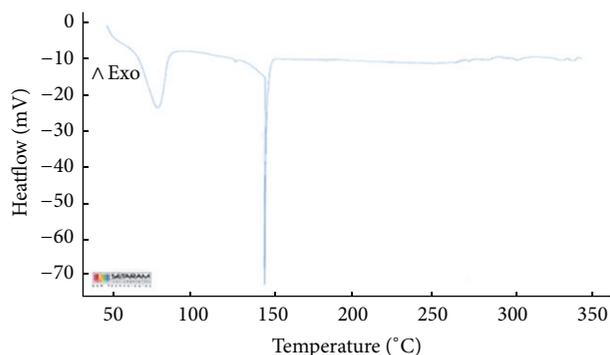


FIGURE 8: DSC curve of $2C_{13}H_{12}N_2O \cdot H_2O$.

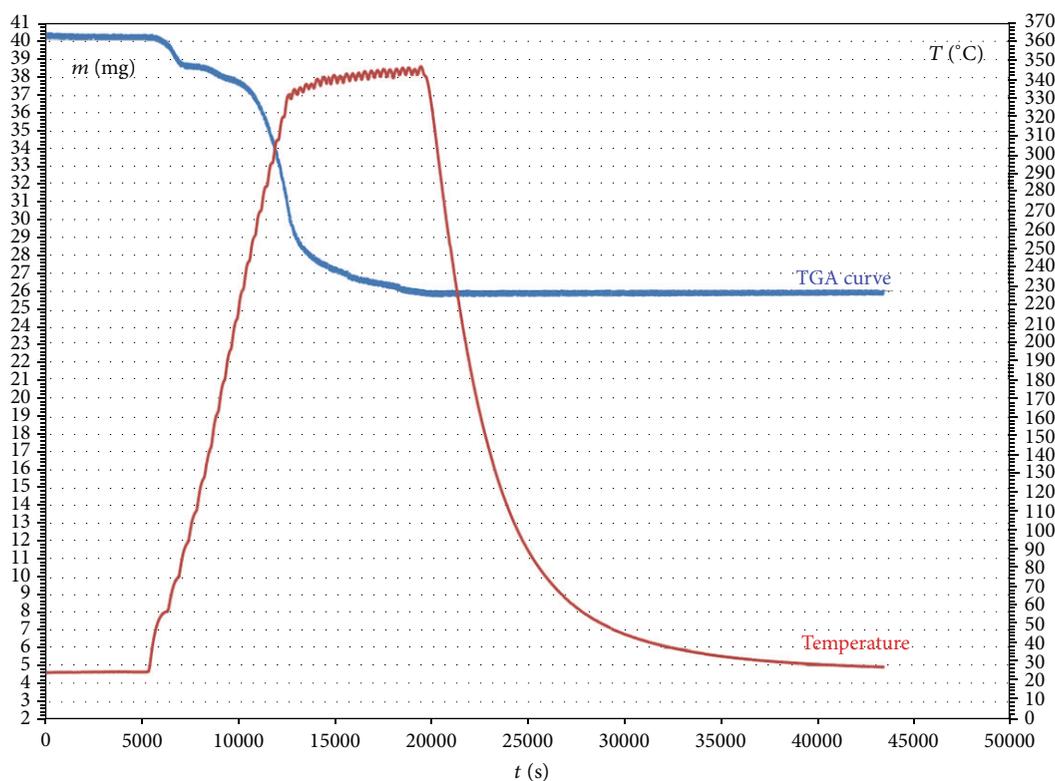


FIGURE 9: TG curve of $2C_{13}H_{12}N_2O \cdot H_2O$.

under controlled atmosphere and led to complimentary results.

3.5.1. Differential Scanning Calorimetry. The DSC curve obtained in the temperature range of $[50^\circ\text{C}, 350^\circ\text{C}]$ and under nitrogen atmosphere reveals two endothermic phenomena (Figure 8). The first one happening at 80°C is due to the compound dehydration. The second one at 140°C is probably due to the departure of ammonia and carbon dioxide as shown by the TGA investigations.

3.5.2. Thermogravimetric Analysis. The thermogravimetric curve analysis of the title compound (Figure 9) was obtained with heating rate of $50^\circ\text{C}\cdot\text{h}^{-1}$, under argon atmosphere in

temperature range (25°C – 300°C). It shows two mass losses. The first $[4.13\% \pm 0.15\%]$ happening at 80°C was attributed to the departure of the water molecule (theoretical value: 4.09%). The second mass loss $[31.05\% \pm 0.27\%]$ beginning around 140°C can be explained by the departure of four ammonia and two carbon monoxide molecules result of the product decomposition (theoretical value: 28.02%).

4. Conclusion

We have synthesized in the present work a new organic compound $2C_{13}H_{12}N_2O \cdot H_2O$. A single crystal X-ray diffraction was carried out in order to solve the structure and to perform structural analysis. This compound has been characterized by IR vibrational spectroscopy. The semiempirical PM3

treatment allows the IR vibrational frequencies calculations. The observed crystal morphology was compared to the simulated one obtained by the Bravais-Friedel, Donnay-Harker model. Calorimetric and thermal studies were carried out to investigate the thermal behaviour of the studied phase. Photoluminescence tests are planned to value this compound.

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