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# Crystal structure, IR spectroscopic and optical properties of the two $(C_{11}N_4H_{10})_4 \cdot H_2O$ and $(C_{11}N_4H_{10})_2 \cdot H_2O$ compounds



CrossMark

Amira Derbel<sup>a</sup>, Issam Omri<sup>a</sup>, Fatma Allouch<sup>b</sup>, Asma Agrebi<sup>b</sup>, Tahar Mhiri<sup>a</sup>, Mohsen Graia<sup>c,\*</sup>

<sup>a</sup> Laboratoire physico-chimie de l'état solide, Faculté de Sciences, Université de Sfax, BP 1171, Route de Soukra, 3038 Sfax, Tunisia <sup>b</sup> Laboratoire de chimie appliquée, hétérocycles, corps gras et polymères, Faculté des Sciences, Université de Sfax, Sfax, Tunisia <sup>c</sup> Laboratoire de Matériaux et Cristallochimie, Faculté des Sciences, Université de Tunis El Manar, El Manar, 2092 Tunis, Tunisia

### HIGHLIGHTS

- $\bullet$  The  $(C_{11}N_4H_{10})_2\cdot H_2O$  and  $(C_{11}N_4H_{10})_4\cdot H_2O$  are a three synthesized organic compounds.
- The two compounds (I) and (II) crystallize in monoclinic system.
- The spectroscopic properties were studied by infrared spectroscopy.
- The cohesion is provided by hydrogen bonds and by Van der Waals interactions.

### G R A P H I C A L A B S T R A C T



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### ABSTRACT

The crystallization of  $(C_{11}N_4H_{10})_2 \cdot H_2O$  (I) and  $(C_{11}N_4H_{10})_4 \cdot H_2O$  (II) is made by slow evaporation from aqueous solutions. The structures of these compounds have been solved and refined by single-crystal X-ray diffraction data. The compound (I) is centrosymmetric (space group C2/c) with lattice parameters: a = 14.118 (2) Å, b = 7.399 (1) Å, c = 21.982 (3) Å and  $\beta = 107.80$  (1)°. The compound (II) crystallizes in the same space group (C2/c) with lattice parameters: a = 28.976 (2) Å, b = 7.593 (2) Å, c = 21.724 (2) Å and  $\beta = 115.819$  (2)°. The cohesion in both structures is provided by two types of bonds: hydrogen bonds O—H···N and N—H···O involving water molecules and organic molecules, and Van der Waals bonds for the connection between the organic molecules. The IR spectra shows an enlargement of the band between 3300 and 2800 cm<sup>-1</sup>, due to the presence of water molecules and the overlap of vibration modes v (O—H) and v (C—H, N—H). The optical band gap is determined to be 4.07 eV by UV–Vis–T90+ absorption spectra, which revealed the nature of insulator.

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### Introduction

Pyrazoles derivatives constitute an important family of compounds due to their applications as pharmaceuticals, agrochemicals and dyestuffs [1–3]. Several pyrazoles have been designed and

\* Corresponding author. Tel.: +216 98938355. *E-mail address:* mohseng2002@yahoo.fr (M. Graia).

http://dx.doi.org/10.1016/j.molstruc.2014.09.009 0022-2860/© 2014 Published by Elsevier B.V. tested as xanthine oxidase inhibitors [4], anti-inflammatory analgesics [5] and herbicides [6]. These heterocyclic compounds are also important and useful as starting materials for the synthesis of other fused heterocyclic pyrazolopyrimidine derivatives of considerable chemical and pharmacological importance [7–9]. Our research interest covers the structural, vibrational, bonding, thermal and other physico-chemical properties of pyrazoles compounds as transition metal complexes with pyrazole-based ligands [10–19]. The



Scheme 1.



Fig. 1. Single crystals of  $(C_{11}N_4H_{10})_2 \cdot H_2O$  (a) and  $(C_{11}N_4H_{10})_4 \cdot H_2O$  (b).

### Table 1

Crystallographic data for the compounds (I) and (II).

Compound	$(C_{11}N_4H_{10})_2 H_2O(I)$	$(C_{11}N_4H_{10})_4 H_2O$ (II)
Empirical formula	C <sub>22</sub> N <sub>8</sub> H <sub>22</sub> O	C <sub>44</sub> N <sub>16</sub> H <sub>42</sub> O
Formula weight (g mol <sup>-1</sup> )	414.48	810.94
Temperature (K)	293	293
Wavelength (Å)	$\lambda = 0.71073$	$\lambda = 0.71073$
Crystal system. Space group	Monoclinic, C2/c	Monoclinic, C2/c
Unit cell dimensions	<i>a</i> = 14.118 (5) Å	a = 28.976 (5) Å
	<i>b</i> = 7.399 (5) Å	b = 7.593 (2) Å
	c = 21.982 (5) Å	c = 21.724 (6) Å
	$\beta = 107.801 \ (5)^{\circ}$	$\beta = 115.82 \ (2)^{\circ}$
Volume (Å <sup>3</sup> )	2186.3 (17)	4302.4 (18)
Z, calculated density (g cm <sup>-3</sup> )	4, 1.259	4, 1.252
F(000)	872	1704
Theta range for data collection	3.1–27.0°	2.1–25.0°
Limiting indices	$-18 \leqslant h \leqslant 18, -9 \leqslant k \leqslant 7, -28 \leqslant l \leqslant 23$	$-34 \leq h \leq 34, -9 \leq k \leq 1, -25 \leq l \leq 25$
No. of reflections collected	7536	8029
No. of independent reflections	2382 $[R_{int} = 0.022]$	3781 [ <i>R</i> <sub>int</sub> = 0.038]
Goodness-of-fit on F <sup>2</sup>	1.05	0.96
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.040; \ wR = 0.123$	$R_1 = 0.045; wR = 0.114$
Parameters	270	290
$\Delta  ho_{ m max}/\Delta  ho_{ m min}$ (e Å $^{-3}$ )	0.12/-0.14	0.17/-0.13
Measurement	Bruker APEX II Kappa CCD	Enraf-Nonius CAD-4
CCDC deposit number	978329	934988

aim of this work is to explain how water molecules stabilize these two pyrazoles compounds. In addition, a large segment of the global economy is based on the use of natural and synthetic zeolites in chemical industries as detergents, adsorbents/descants and heterogeneous catalysts [20–23].

In this paper we are interested to study IR spectroscopy and structural X-ray diffraction on a single crystal of two new compounds corresponding to the same organic base, 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile and two different degrees of hydration:  $(C_{11}N_4H_{10})_2 \cdot H_2O$  (I) and  $(C_{11}N_4H_{10})_4 \cdot H_2O$  (II). In order to compare its IR spectroscopies with that of the

analog and verify the new synthesis method, compound  $(C_{11}N_4H_{10})$  was also synthesized and characterized.

### Experimental

*Preparation of the three compounds* 

Preparation of the organic  $(C_{11}N_4H_{10})$  compound

A mixture of phenyl hydrazine (33 mmol) and ethoxymethylene malononitrile (33 mmol) was heated at reflux for 2 h in ethanol

### Table 2

Principal intermolecular distances (Å) and angles (°) in for the two  $(C_{11}N_4H_{10})_2 \cdot H_2O$  and  $(C_{11}N_4H_{10})_4 \cdot H_2O$  compounds.

= (=11:.4-10)4 - 2 =P				
$(C_{11}N_4H_{10})_2 \cdot H_2O(I)$		$(C_{11}N_4H_{10})_4 \cdot H_2O$ (II)		
Bond length (Å)				
C1A–C6A	1.3900	C1-C6	1.379 (3)	
C1A-C2A	1 3900	$(1-0)^{-1}$	1 383 (3)	
N1A_C1A	1 /13 (3)	C1_N1	1.303 (3)	
	1.415 (5)		1.423 (2)	
CZA-C3A	1.3900	(2-(3	1.388 (3)	
C3A–C4A	1.3900	C3–C4	1.378 (4)	
C4A—C5A	1.3900	C4—C5	1.367 (4)	
C5A–C6A	1.3900	C5–C6	1.380 (3)	
N3A—C9A	1.333 (8)	C7—N3	1.352 (2)	
C9A-C8A	1404(7)	7 - 68	1 391 (2)	
	1.40(1)	C7 N1	1.351(2)	
	1.40(1)	C7—N1	1.354 (2)	
C8A-C7A	1.400 (6)	68-69	1.407 (3)	
C7A-C10A	1.495 (7)	C8–C11	1.405 (3)	
N4A–C11A	1.08 (2)	C9-N2	1.317 (2)	
N2A-C7A	1.305 (5)	C9–C10	1.495 (3)	
N2A—N1A	1 393 (4)	N1-N2	1 395 (2)	
N1A COA	1.555 (1)	C11 N4	1.333(2)	
NIA-COA	1.552 (0)		1.144 (2)	
N3B-C9B	1.351 (7)	C12-C13	1.373 (3)	
N2B-C7B	1.316 (5)	C12–C17	1.380 (3)	
N2B-N1B	1.386 (4)	C12-N5	1.431 (2)	
N1B-C9B	1.351 (6)	C13–C14	1.383 (3)	
N1B-C1B	1 416 (3)	C14-C15	1 384 (3)	
	1 201 (7)	C15_C16	1 264 (4)	
C9D-C8B	1.301 (7)		1.304 (4)	
C8B-C7B	1.410 (6)	C16-C17	1.380 (3)	
C8B-C11B	1.43 (1)	C18—N5	1.355 (2)	
C7B-C10B	1.475 (8)	C18–N7	1.361 (2)	
N4B-C11B	1.23 (2)	C18–C19	1.385 (2)	
C1B-C2B	1 3900	C19-C22	1 413 (3)	
C1P_C6P	1 2000	$C_{10}$ $C_{20}$	1 407 (2)	
CIB-COB	1,3900	C19-C20	1.407 (3)	
C2B-C3B	1.3900	C20—N6	1.315(2)	
C3B-C4B	1.3900	C20–C21	1.493 (3)	
C4BC5B	1.3900	N5—N6	1.387 (2)	
C5B-C6B	1.3900	C22-N8	1.146 (2)	
Bona angle (°)				
C7A—N2A—N1A	105.9 (3)	C6-C1-C2	120.6 (2)	
C9A-N1A-N2A	111.4 (3)	C6-C1-N1	120.51 (19)	
C9A-N1A-C1A	129.7 (3)	C2-C1-N1	118.9 (2)	
N2A-N1A-C1A	1188(3)	$C_{3} = C_{2} = C_{1}$	1188(3)	
	110.0 (5)		120.2 (2)	
N3A-C9A-NTA	120.1 (0)	(2-(3-(4	120.3 (3)	
N3A-C9A-C8A	128.6 (6)	C5-C4-C3	120.4 (2)	
N1A-C9A-C8A	105.2 (4)	C4—C5—C6	120.0 (3)	
C11A–C8A–C7A	127.4 (5)	C5-C6-C1	119.9 (2)	
C11A-C8A-C9A	125.9 (5)	N3-C7-C8	129.26 (18)	
C7A-C8A-C9A	1064(5)	N3-C7-N1	124 77 (17)	
N2A_C7A_C8A	1110(4)	C8-C7-N1	105.04(17)	
	111.0(4)		105.54 (17)	
NZA-C/A-CIUA	121.4 (4)	07-08-09	105.92 (16)	
C8A-C/A-CIUA	127.5 (5)	C/-C8-C11	125.87 (18)	
N4A-C11A-C8A	167.1 (15)	C9–C8–C11	128.20 (18)	
C2A-C1A-C6A	120.0	N2-C9-C8	111.54 (17)	
C2A-C1A-N1A	119.38 (16)	N2-C9-C10	121.10(17)	
C6A—C1A—N1A	120 62 (16)	C8-C9-C10	127 36 (18)	
$C_{3}$ $C_{2}$ $C_{3}$ $C_{3$	120.02 (10)	C7_N1_N2	111 70 (15)	
	120.0	C7 N1 N2	120.21 (17)	
CZA-C3A-C4A	120.0	C/-NI-CI	129.31 (17)	
C5A-C4A-C3A	120.0	N2-N1-C1	118.82 (15)	
C6A—C5A—C4A	120.0	C9-N2-N1	104.88 (15)	
C5A-C6A-C1A	120.0	N4-C11-C8	179.3 (3)	
C7B—N2B—N1B	105.4 (3)	C13–C12–C17	120.6 (2)	
C9B-N1B-N2B	1112 (3)	C13-C12-N5	1188(2)	
CQR_N1R_C1P	131 2 (3)	C17_C12_N5	120 51 (10)	
	1175 (3)	C12 C12 C14	110 2 (2)	
	117.3 (2)	C12-C13-C14	119.2 (2)	
N1B-C9B-N3B	123.8 (6)	C15-C14-C13	120.3 (2)	
N1B-C9B-C8B	106.7 (4)	C14-C15-C16	120.0 (2)	
N3B-C9B-C8B	129.5 (6)	C17-C16-C15	120.3 (2)	
C9B—C8B—C7B	105.6 (4)	C12-C17-C16	119.7 (2)	
C9B-C8B-C11B	1280(5)	N5-C18-N7	122.98 (17)	
C7B_C8P_C11P	126.4 (5)	N5_C19_C10	105 00 (17)	
	120.7 (J)	N7 C10 C10	103.30 (17)	
INZB-C/B-C8B	111.2 (4)	IN/	131.04 (18)	
N2B-C7B-C10B	121.6 (4)	C22-C19-C20	125.99 (18)	
C8B-C7B-C10B	127.2 (5)	C22-C19-C18	127.99 (18)	
N4B-C11B-C8B	171.5 (13)	C20-C19-C18	105.98 (16)	
C2B-C1B-C6B	120.0	N6-C20-C19	111.26 (17)	
C2B-C1B-N1B	1191(2)	N6-C20-C21	121 30 (18)	
	120.0 (2)	C10_C20_C21	127.30 (10)	
COD-CID-INIB	120.9 (2)	LIJ-L20-L21	127.41(18)	

Table 2 (continued)

· · · ·			
$(C_{11}N_4H_{10})_2{\cdot}H_2O\;(I)$		$(C_{11}N_4H_{10})_4 \cdot H_2O$ (II)	
C3B-C2B-C1B C4B-C3B-C2B C3B-C4B-C5B C4B-C5B-C6B	120.0 120.0 120.0 120.0 120.0	C18—N5—N6 C18—N5—C12 N6—N5—C12 C20—N6—N5	111.58 (15) 129.85 (17) 118.48 (15) 105.18 (15)
C5B-C6B-C1B	120.0	N8-C22-C19	177.5 (2)



Fig. 2. IR spectra of the  $(C_{11}N_4H_{10}),\ (C_{11}N_4H_{10})_2\cdot H_2O$  and  $(C_{11}N_4H_{10})_4\cdot H_2O$  compounds.

(30 mL). The product, which precipitates, was filtered and recrystallized from ethanol (Scheme 1).

5-Amino-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile is synthesized as mentioned in literature [24].

### Preparation of the $(C_{11}N_4H_{10})_2 \cdot H_2O$ compound

 $V_2O_5$  (0.091 g) was dissolved in solution of oxalic acid (0.252 g in 15 mL of H\_2O and 1 ml of H\_2O\_2 (30%)). Solution of 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile (0.198 g) in 10 mL of ethanol was added under continuous stirring. White crystals of about  $0.25\times0.25\times6~mm^3$  were isolated after a few weeks (Fig. 1a).

### Preparation of the $(C_{11}N_4H_{10})_4 \cdot H_2O$ compound

A mixture consisting of 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile (0.02 g) and NiCl<sub>2</sub> (0.02 g) in ethanol (5 mL) was added to a solution of  $As_2O_3$  (0.04 g) and  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.25 g) in 5 mL of water under continuous stirring. The mixture is stirred with a little heat for 30 min, by using pH paper. We note that the solution is neutral, then we add a few drops of NaOH up

Assignment	IR wavenumber v (cm <sup>-1</sup> )	IR wavenumber v (cm <sup>-1</sup> )			
	(C <sub>11</sub> N <sub>4</sub> H <sub>10</sub> )	$(C_{11}N_4H_{10})_2 \cdot H_2O$	$(C_{11}N_4H_{10})_4 \cdot H_2O$		
$v_{as}$ (NH <sub>2</sub> )	3333	3330	3329		
$v_{s}$ (NH <sub>2</sub> )	3226	3228	3228		
v (CH) aromatic	3198	3194	3198		
$v_{s}$ (C $\equiv$ N)	2218	2218	2215		
ν (C=C). ν (C=N)	1643, 1595, 1565, 1534, 1489, 1455, 1412	1639, 1596, 1561, 1536, 1484, 1456, 1410	1652, 1595, 1563, 1533, 1488, 1442, 1410		





**Fig. 3.** (a) View of asymmetric unit in  $(C_{11}N_4H_{10})_2$ · $H_2O$  along the *b*-axis and (b) view of asymmetric unit  $(C_{11}N_4H_{10})_4$ · $H_2O$  along the *b*-axis.



**Fig. 4.** (a) Projection along the *b*-axis of the structure in compound (I) and (b) projection along the *b*-axis of the structure in compound (II). The drawing shows the intermolecular hydrogen bonds contacts which are represented by dotted line.

reach pH = 12. White crystals of about  $0.40 \times 0.40 \times 2.3 \text{ mm}^3$  were obtained after one week (Fig. 1b).

## at room temperature using a T90+–UV–Vis spectrometer within the range of 300–700 nm. BaSO<sub>4</sub> was used as a reference material.

### Spectroscopy analysis

The infrared spectrum was recorded at room temperature on a Perkin Elmer Spectrum™ 100 FT-IR spectrometer in the 4000–400 cm<sup>-1</sup> region. The Optical absorption spectra were measured

### X-ray crystallography

A suitable single crystal of each compound was chosen for the structure determination and refinement. It was selected under a polarizing microscope and was mounted on a glass fiber. The



**Fig. 5.** (a) A layer structure of compound  $(C_{11}N_4H_{10})_2$ ·H<sub>2</sub>O and (b) a layer structure of compound  $(C_{11}N_4H_{10})_4$ ·H<sub>2</sub>O.



Fig. 6. Connection between organic molecules via H<sub>2</sub>O molecules (OH···N and NH···O interactions) in compound (I), and by NH···N hydrogen bonds in compound (II).



**Fig. 7.** Distances between rings in the structure of the two compounds (I) and (II) ( $a^{1}$ : 3/2 - x, 1/2 + y, 1/2 - z;  $^{b}$ : x, 1 + y, z;  $^{c}$ : x, y, 1 - z; Ph: Phenyl; Pz: pyrazole).

 $(C_{11}N_4H_{10})_2 H_2O$  compound is collected at room temperature using a Bruker APEX II Kappa CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation [25]. In each of the studied phases, the crystal structure was solved and refined against  $F^2$  using the SHELX-97 computer programs [26,27] included in the WingX software package [28]. The organic cations in the structure of (I) have

Table 4
Distances and dihedral angles of the two compounds (I) and (II)

$(C_{11}N_4H_{10})_2 \cdot H_2O$	$(C_{11}N_4H_{10})_4 \cdot H_2O$
Distances (Å)	
	$Ph1^{c}-Pz2 = 3.777$
$Ph1^{b}-Pz1^{a} = 3.654$	$Pz1^{c}-Ph2 = 3.747$
$Pz1^{b}-Ph1^{a} = 3.804$	Pz2-Ph1 = 3.825
	Ph2-Pz1 = 3.859
$Ph1^{b}-Ph1^{a} = 5.181$	$Ph1^{c}-Ph2 = 6.078$
$Pz1^{b}-Pz1^{a} = 5.642$	Ph2-Ph1 = 4.947
	$Pz1^{c}-Pz2 = 4.706$
	Pz2-Pz1 = 5.986
Angles (°)	
$Ph1^{b}-Pz1^{a} = 7.066$	$Ph1^{c}-Pr2 = 3.364$
$P_{71}^{b} P_{71}^{b} = 7.066$	$P_{7}^{1} = 122 = 5.504$
F21 -FIII - 7.000	FZ1 -F112 - 5,151
$Ph1^{b}-Pz1^{b} = 34.847$	$Ph1^{c}-Pz1^{c} = 39.109$
$Pz1^{a}-Ph1^{a} = 34.847$	Pz2–Ph2 = 39.577

Ph: Phenyl; Pz: Pyrazole.

<sup>a</sup> 3/2 - x, 1/2 + y, 1/2 - z.

<sup>b</sup> x, 1 + y, z.

<sup>c</sup> x, y, 1 - z.

occupancy disorders in adjacent positions. These disorders have been resolved and have refined the occupancy rates of partially different occupied sites by using the tools available in the SHELXL97 [29] software. For clarity of structure (I) we should represent a single position. The crystal structure of the  $(C_{11}N_4H_{10})_4$ ·H<sub>2</sub>O compound is determined from single-crystal X-ray diffraction data collected at room temperature using an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation [30]. The reflections were corrected for Lorentz and polarization effects; absorption correction was obtained via a psi-scan [31] and secondary extinction correction was applied too [26].

Experimental conditions used for the intensity data collection and the refinement results are listed in Table 1. All atoms were refined with anisotropic thermal parameters. The significant bond lengths and angles are listed in Table 2. The atomic coordinates and the displacement parameters are reported in Tables S1–S4 (Supplementary materials).

The cell parameters of two compounds are almost similar. Indeed, the two compounds crystallizes in the monoclinic system with  $\beta$  angles fairly close and such as *b* and *c* parameters are practically the same, while the *a* parameter of the compound (II) is double that of the compound (I). This is explained by the decline in symmetry that accompanies the resulting vacancy of water molecules in compound (II).

The comparison of volumes per formulary unit shows that the compound (I) has a larger volume than in compound (I). This gap

Table 6		

Tuble 0				
Hydrogen-bond	geometry of the	two compounds	(I) and	(II).

D—H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<d—h…a< th=""></d—h…a<>
$(C_{11}N_4H_{10})_2 \cdot H_2O$				
OW1-HW1N2A	0.96	1.98	2.917	164.8
OW1-HW1N2B	0.96	1.90	2.857	175.4
N3A—H3A1…N4A <sup>a</sup>	0.85	2.17	3.010	172
N3A—H3A2…OW1 <sup>b</sup>	1.14	1.87	2.997	170
C6A—H6A…N3A	0.93	2.58	3.063	113
N3B—H3B1…N4B <sup>a</sup>	0.87	2.60	3.29	137
C6B—H6B…N3B	0.93	2.53	3.042	115
$(C_{11}N_4H_{10})_4 \cdot H_2O$				
N7–H7A···N8 <sup>c</sup>	0.941	2.134	3.073	175.37
N7—H7B· · · N2 <sup>d</sup>	0.877	2.370	3.177	152.96
N3–H3A···OW1	0.941	2.185	3.103	164.94
N3—H3B· · · N4 <sup>e</sup>	0.913	2.226	3.132	172.03
$OW1-HW\cdots N6^{f}$	0.953	1.977	2.923	171.47

<sup>a</sup> -x + 3/2, -y + 1/2, -z.

<sup>b</sup> x + 1/2, y + 1/2, z.

<sup>c</sup> -x + 1/2, -y - 1/2, -z.

<sup>d</sup> x, y - 1, z.

e -x, -y + 1, -z - 1.

f -x, y, -z - 1/2.

is 17.55  $Å^3$  per water molecule. It corresponds well to the occupied volume by this molecule in the crystal structures.

### **Result and discussion**

### Infrared spectroscopy

The spectrum of the compound (I) and (II) shows bands at 3329 cm<sup>-1</sup> assigned to an asymmetric NH<sub>2</sub> stretching band. The characteristic band at 3228 cm<sup>-1</sup> is assigned to a symmetric NH<sub>2</sub> stretching band [32–34]. The aromatic structure shows the presence of C-H stretching vibration in the characteristic region 3100–3000 cm<sup>-1</sup> [35]. The band arising from v (C $\equiv$ N) was observed at 2216 cm<sup>-1</sup> [32,33]. The most characteristic bands are those at  $1653-1410 \text{ cm}^{-1}$ , attributable to the pyrazole C=C and C=N groups [32-34]. The band in the 1080–1000 cm<sup>-1</sup> region has been assigned to the pyrazole N—N group [36]. For pyrazoles, it must be indicating that a lone pair of nitrogen N in the NH<sub>2</sub> group is conjugated with the pyrazole ring. These justify the decrease of the N-H vibration band (3329 cm<sup>-1</sup>, 3228 cm<sup>-1</sup>). Whereas, for primary amines N–H vibrates between 3400 cm<sup>-1</sup> for symmetric stretching and 3500 cm<sup>-1</sup> for asymmetric stretching (Fig. 2, Table 3). The three spectra exhibit the same attributed band of each spectrum peak. While the IR spectra of the two compounds (I) and (II) shows an enlargement of the band between 3300 and 2800 cm<sup>-1</sup>, due to the presence of water molecules and the overlap of vibration modes v (O–H) and v (C–H, N–H).

### Table 5

Distances and bond angles of the two compounds (I) and (II).

Compound (I)		Compound (II)	
N3Ab	N <sub>3</sub> A <sup>b</sup> —OW <sub>1</sub> —N <sub>3</sub> A = 122.51°	N3a N3 N6a	$N_3 - OW_1 - N_3^a = 116.8^\circ$
OW1 IN N2Ab	N <sub>3</sub> A <sup>b</sup> —OW <sub>1</sub> —N <sub>2</sub> A = 100.64°		$N_3 - OW_1 - N_6 = 98.8^\circ$
$\begin{array}{l} OW_1 - N_2 A = 2.917 \ \text{\AA} \\ OW_1 - N_2 A^{\text{b}} = 2.917 \ \text{\AA} \\ OW_1 - N_3 \text{\AA}^{\text{b}} = 2.997 \ \text{\AA} \end{array}$	$N_3A^b - OW_1 - N_2A^b = 105.94^\circ$	$OW_1 - N_6 = 2.923 \text{ Å}$	$N_3$ -OW <sub>1</sub> -N <sub>6</sub> <sup>a</sup> = 118.5°
	$N_3A - OW_1 - N_2A^b = 100.64^\circ$	$OW_1 - N_6^a = 2.923 \text{ Å}$	$N_3^a$ -OW <sub>1</sub> -N <sub>6</sub> <sup>a</sup> = 98.8°
	$N_3A - OW_1 - N_2A = 105.94^\circ$	$OW_1 - N_3 = 3.104 \text{ Å}$	$N_3^a$ -OW <sub>1</sub> -N <sub>6</sub> = 118.5°
$OW_1 - N_3 A = 2.997 \text{ Å}$	$N_2A^{D}-OW_1-N_2A = 122.95^{\circ}$	$OW_1 - N_3^{d} = 3.104 \text{ Å}$	$N_6^{d} - OW_1 - N_6 = 105.7^{\circ}$

 $a^{a} -x, y, -z - 1/2.$ 

<sup>b</sup> 1 - x, y, 1/2 - z.

### Structural study

The asymmetric units of the compounds (I) and (II) have one and two organic molecules 5-amino-3-methyl-1-phenyl-1H-pyrazole-4-carbonitrile, respectively. In each compound the OW water molecule is localized in only one special position (Fig. 3).

These compounds have the same structural arrangement. In fact, the two structures can be described as a succession of layers interconnected by NH $\cdots$ N (Fig. 4). In these layers, the organic molecules are stacked into ribbons parallel to *b* axis. And each of water molecules can connect four adjacent organic groups, leading to a tetrahedral environment of the oxygen atom. Inter-atomic distances in molecules are comparable with those in similar compounds [37–40].

In the compound (I), each of the organic molecules is connected by two water molecules, allowing the progression of layers according to *a* and *b* axis (Fig. 5a). In fact, the water molecules alternate with organic groups and allow the formation of a three-dimensional framework. On the contrary, in the compound (II), water molecules contribute to the cohesion of organic molecules along *b* axis whereas along *a* axis no connection was observed. In this structure NH···N bonds permit the formation of dimers of organic molecules (Fig. 6). Thereby, each water molecule connects two dimers of organic molecules. This lead to the formation of equivalent ribbons that are not directly related together (Fig. 5b). Fig. 7 presents the stack of organic molecules according to the b axis in each compound. This figure shows that adjacent molecules in compound (II) are crystallographically not equivalent.

The distances and dihedral angles of the two compounds are listed in Table 4. This table shows that intermolecular distances are comparable in these rows, which allows the interactions energies between molecules have the same range. The  $\pi \cdots \pi$  interactions between two adjacent rings (Ph–Pz) is between 3.654 Å and 3.859 Å [41].

In the compound (II) the ring centroid-to-centroid distance Pz1<sup>c</sup>–Pz2 (in the dimer group: 4.706 Å) is shorter than to the second Pz2–Pz1 distance (between adjacent dimer groups: 5.986 Å) and those of Pz–Pz (5.642 Å) in compound (I). This is due to the formation of dimers by an intramolecular NH···N hydrogen bond (Fig. 7).

In the two studied compounds, water molecules lie in layers and contribute to their cohesion (Fig. 4). In fact, each water molecule is surrounded by four organic molecules and allows its connections by two NH···O hydrogen bonds and two OH···N hydrogen bonds (Fig. 5). These bonds lead to a distorted tetrahedron environment to OW atom (Table 5). The Table 6 shows that all the hydrogen bonds are weak based on the criteria of Brown [42].

Finally, we note that the formation of  $N_2 \cdots N_7 H$  hydrogen bond in compound (II) is accompanied by two important modifications in the structure. On the one hand, a lateral displacement of the



Fig. 8. (a) UV-Vis absorption spectrum of (I) and (II) taken at room temperature, (b) determination of the optical band gap of compound (I) by UV-Vis absorption spectrum and (c) determination of the optical band gap of compound (II) by UV-Vis absorption spectrum.

molecules (1) and (3) relative to (2) is observed. This displacement led to the shortening of the distance Pz1<sup>c</sup>-Pz2 against an elongation of distance Pz2-Pz1 (Table 4). On the other hand, in the molecule (1), there is a rotation of angle (169.38°) around the bond  $C_1$ - $N_1$  compared to that of structure (I). This rotation allowed the shortening of the  $N_2$ - $N_7$  distance to a favorable value to the hydrogen bonding interaction (Fig. 7, Table 4).

### **Optical properties**

The room-temperature UV–Vis absorption spectra of (I) and (II) are given in Fig. 8 and indicate characteristic excitonic absorption. Excitonic absorptions at 256, 267 and 280 nm for the two compounds can be observed. The absorption peaks at around 280 nm can be attributed to  $n-\pi^*$ , but the absorption peaks at 256 and 267 nm are assigned to  $\pi-\pi^*$ .

The optical band gap of two compounds is 4.07 eV, showing their insulator nature (the values of *Eg* were obtained with the use of a straightforward extrapolation method).

### Conclusion

The IR spectra of the three compounds  $(C_{11}N_4H_{10})$ ,  $(C_{11}N_4H_{10})_2$ .  $\cdot$ H<sub>2</sub>O (I) and  $(C_{11}N_4H_{10})_4$ ·H<sub>2</sub>O (II) presents a sharp resemblance. Whereas, the IR spectra of the two compounds (I) and (II) shows an enlargement of the band between 3300 and 2800 cm<sup>-1</sup>, due to the presence of water molecules and the overlap of vibration modes v (O–H) and v (C–H, N–H).

In the structures of compounds (I) and (II), the organic molecules arrange into parallel layers. Also, in the space inter-layers the water molecules are localized. The compound (I) has  $H_2O$  molecules which alternate with organic groups; it allows the formation of a three-dimensional framework. While in the compound (II) the water molecules are not always present. Indeed, the corresponding sites are occupied once on two and it has established a new  $N_7H\cdots N_2$  hydrogen bond between two adjacent groups which allows the formation of dimers in these ribbons. It results in the shortening of distances between Ph–Pz groups in dimer against growing of distances between Pz–Ph groups from two neighboring dimers. These ribbons are formed as a two-dimensional structure.

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### **Appendix A. Supplementary material**

CCDC 978329 and 934988 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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; or e-mail: deposit@ccdc.cam.ac.uk.

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