



## Synthesis and characterization of a new noncentrosymmetric dihydrogenmonophosphate $[C_3H_6N_3S_2]H_2PO_4$

M. L. Mrad<sup>1</sup>, K. Chair<sup>1</sup>, S. Ammar<sup>2</sup>, E. Jeanneau<sup>3</sup>, F. Lefebvre<sup>4</sup> and C. Ben Nasr<sup>1,\*</sup>

<sup>1</sup>Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 - Zarzouna - Bizerte Tunisie.

<sup>2</sup>Faculté des Sciences de Gabes, Tunisie

<sup>3</sup>Centre de Diffractométrie Henri Longchambon, Université Claude Bernard Lyon 1, Villeurbanne Cedex, France.

<sup>4</sup>Laboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, Villeurbanne Cedex, France.

### ARTICLE INFO

#### Article history:

Received: 11 April 2012;

Received in revised form:

30 September 2012;

Accepted: 4 October 2012;

#### Keywords

X-ray diffraction,  
Infrared Spectroscopy,  
NMR Spectroscopy,  
DFT calculations.

### ABSTRACT

The crystal structure of the title organic-inorganic hybrid material  $[C_3H_6N_3S_2]H_2PO_4$ , has been determined by single crystal X-ray diffraction. The compound crystallizes in the noncentrosymmetric orthorhombic space group  $Pna2_1$  with the lattice parameters  $a = 7.662$  (1),  $b = 26.553$  (3),  $c = 4.4258$  (6) Å,  $V = 900.4$  (2) Å<sup>3</sup>, and  $Z = 4$ . The framework is built upon layers parallel to (0 1 0) made up from  $H_2PO_4^-$  entities associated by O---H...O strong hydrogen bonds. The organic cations are located between the layers and connect them via N-H...O and C-H...O hydrogen bonding network. The exocyclic C-N bond length reveals the presence of the imine and enamine tautomers in the starting reagent. Results from solid state <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C and <sup>15</sup>N spectroscopy are in good agreement with the X-ray structure. Density functional theory calculations allowed for the assignment of the carbon and nitrogen peaks to the independent crystallographic sites.

© 2012 Elixir All rights reserved.

### Introduction

Organic-inorganic hybrid materials with noncentrosymmetric structures are interesting for their application in various fields such as e.g. quadratic non-linear optical materials research [1]. Their abilities to combine the high cohesion of inorganic host matrices with the enhanced polarizability of organic guest chromophores within one molecular scale leads to a better performance of optical signal-processing devices [2]. The design of organic-inorganic polar crystals for quadratic nonlinear optical applications is supported by two observations. Firstly, the organic molecules containing  $\pi$ -bonds asymmetricized by electron donor-acceptor groups are highly polarizable entities in which transparency could be controlled. Secondly, the ionic inorganic host matrices may increase the packing cohesion, shift the transparency of crystal towards blue wavelengths, and induce noncentrosymmetry.

Within a systematic investigation of new materials resulting from the association of organic chromophores with inorganic species, we report here the synthesis and the characterization of a new dihydrogenmonophosphate,  $[C_3H_6N_3S_2]H_2PO_4$ , including the amine, a chromophore which could be efficient in the blue-U.V. wavelength region. This compound could exhibit a richness of interesting physical properties such as ferroelectricity and nonlinear optic phenomena like second harmonic generation.

### Experimental

#### Chemical preparation

Crystals of the title compound were prepared by slow addition at room temperature, concentrated orthophosphoric acid to an alcoholic solution of 2-amino-5-methylmercapto-1, 3,4, thiazol. The acid is added until the alcoholic solution becomes turbid. After filtration, the solution is slowly evaporated at room temperature during several days until the formation of

transparent prismatic crystals with suitable dimensions for crystallographic study. The crystals are stable for months in normal conditions of temperature and humidity.

#### Investigation techniques

The characterization of these salts was carried out using X-ray diffraction, solid state NMR spectroscopy, DFT calculations, and infrared spectroscopy.

#### X-ray diffraction

A single crystal was carefully selected under a microscope in order to perform its structural analysis by X-ray diffraction. The intensity data were collected on a Bruker AXS S Xcalibur, Atlas, Gemini ultra diffractometer using omega scan technique with  $MoK\alpha$  radiation ( $\lambda = 0.7107$  Å). The structure was solved with direct methods using the SIR97 [3] and refined with full-matrix least-squares techniques using CRYSTALS [4]. The drawings were made with Diamond [5]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

#### NMR spectroscopy

All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 300 MHz for <sup>1</sup>H, 30.30 MHz for <sup>15</sup>N, 75.49 MHz for <sup>13</sup>C, and 121.51 MHz for <sup>31</sup>P, with a classical 4 mm probehead allowing spinning rates up to 10 kHz. <sup>13</sup>C and <sup>1</sup>H NMR chemical shifts are given relative to tetramethylsilane, while the <sup>15</sup>N and <sup>31</sup>P ones are given relative to glycine (at 30.0 ppm) and 85%  $H_3PO_4$ , respectively (external references precision 0.5 ppm). The proton and phosphorous spectra were recorded under classical MAS conditions, while the carbon and nitrogen ones were recorded by use of cross-polarization from protons (contact time 5 ms). A 2D HETCOR <sup>13</sup>C-<sup>1</sup>H NMR spectrum was obtained with a classical sequence and a 5 ms

contact time to ensure a good transfer of the proton magnetization to all nuclei.

### IR Spectroscopy

The spectrum was recorded in the range 4000 - 400  $\text{cm}^{-1}$  with a "Perkin-Elmer FTIR" spectrophotometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet.

### Results and discussion

#### X-ray diffraction study

The title organic-inorganic hybrid material crystallizes in a non-centrosymmetric setting in the chiral space group  $Pna2_1$ . Its structure consists of 2-(methylthio)thiazol-5(4*H*)-iminium cation and one dihydrogenmonophosphate anion (Figure 1). The present atomic arrangement is a typical layered organization as very often encountered in this kind of inorganic-organic hybrid compounds [6]. The  $\text{H}_2\text{PO}_4$  groups interconnected through strong hydrogen bonds form two-dimensional thick layers spreading along the  $y = 0$  plane.

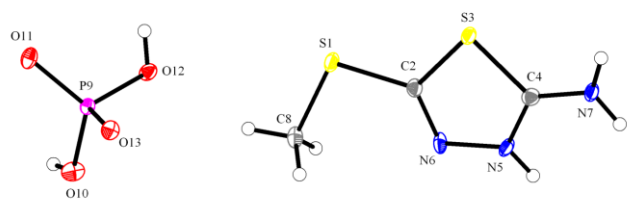


Fig. 1. Ortep view of the asymmetric unit of the  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$ . Thermal ellipsoids are given at 50 % probability

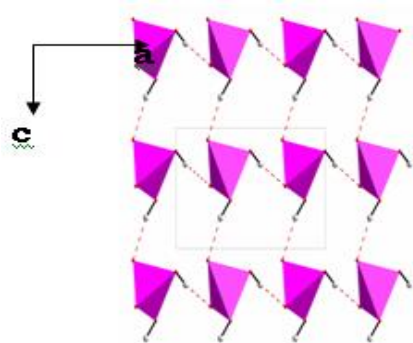


Fig. 2. Projection along the b-direction of the inorganic layer in  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$ . The phosphoric anion is given in polyhedral representation

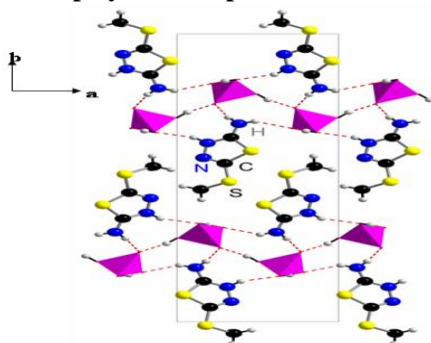


Fig. 3. The atomic arrangement of  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$  in projection along the c-direction. The phosphoric anion is given in polyhedral representation.

Figure 2 reports, in projection along the b direction, the organization of an inorganic layer. Two such layers cross the unit cell at  $z = (2n + 1)/4$  (Fig. 3). The organic entities are anchored to inorganic layers through N-H...O and C-H...O hydrogen bonds whose geometrical characteristics are given in Table 3. The projection of the whole arrangement along the c-axis (Figure 3) shows clearly how these moieties alternate as to fill up the wide space separating two inorganic layers.

The detailed geometry of the  $\text{H}_2\text{PO}_4$  groups shows two kinds of P-O distances. The shortest ones (1.506(2) and 1.509(2) Å) correspond to the phosphorous atom doubly bonded to the oxygen atom, while the largest ones (1.561(2), 1.576(2) Å) can be attributed to the P-OH bond length. This is in agreement with the literature data [7]. Relatively short distances 1.70(2) and 1.71(2) Å, characterize all the H...O bonds, which maintain the cohesion of the arrangement. It is worth noting that the O...O distances involved in hydrogen bonds (2.515(4)-2.531(4) Å), are of the same order of magnitude than the O...O distances in the  $\text{PO}_4$  tetrahedron (2.444-2.570 Å). This could allow us to consider the  $[\text{H}_2\text{PO}_4]_n^{n-}$  subnetwork as a "macroanion" [8].

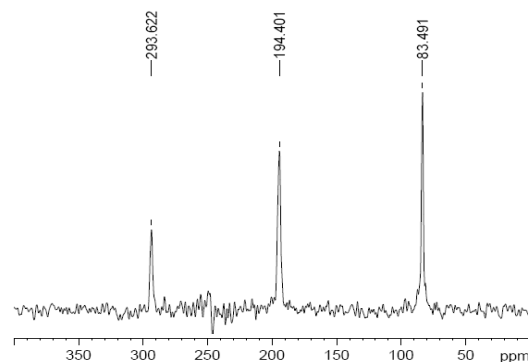


Fig. 4.  $^{15}\text{N}$  CP-MAS-NMR spectrum of  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$

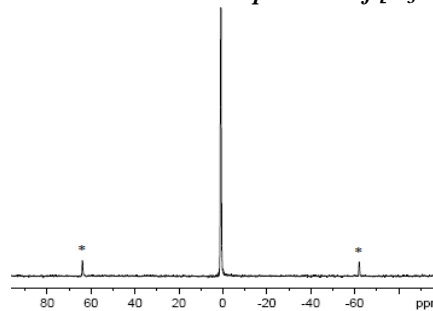


Fig. 5.  $^{31}\text{P}$  MAS-NMR spectrum of  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$ . \* Spinning sidebands

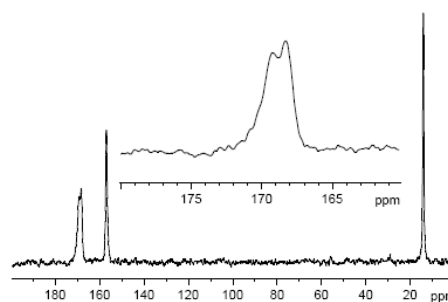


Fig. 6.  $^{13}\text{C}$  CP-MAS-NMR spectrum of  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$ .

Examination of the geometrical features of the organic moiety shows that the C4-N7 bond length [1.312(4) Å] is slightly shorter than that of C4-N5 [1.331(4) Å] which suggests

**Table 1. Crystal data, experimental parameters used for the intensity data collection, strategy, and final results of the structure determination of [C<sub>3</sub>H<sub>6</sub>N<sub>3</sub>S<sub>2</sub>]<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>.**

Empirical Formula	C <sub>3</sub> H <sub>6</sub> N <sub>3</sub> S <sub>2</sub> O <sub>4</sub> P
Formula weight	245.22
Crystal system	Orthorhombic
Space group	: P n a <sub>2</sub> 1
a	7.662(1) Å
b	26.553(3) Å
c	4.4258(6) Å
Z	4
V	900.40(2) Å <sup>3</sup>
ρ <sub>cal.</sub>	1.809 (g. cm <sup>-3</sup> )
F(000)	504
μ(AgK <sub>α</sub> )	0.76 (mm <sup>-1</sup> )
Crystal size [mm]	0.64 x 0.42 x 0.29
Theta range	3°/30°
h, k, l range	-10/10, -33/36, -5/5
Reflections measured	7088
Independent reflections	2138
Unique reflections included ( <i>I</i> > 2σ <i>I</i> )	2109
Refined parameters	120
Δρ <sub>min</sub> /Δρ <sub>max</sub> (e/Å <sup>3</sup> )	-0.61/0.58
R	0.036
R( <i>w</i> )	0.096
Largest shift/error	0.001

The main geometrical features of the different entities are given in Tables 2 and 3.

**Table 2. Main interatomic distances (Å) and bond angles (°) in the inorganic groups of [C<sub>3</sub>H<sub>6</sub>N<sub>3</sub>S<sub>2</sub>]<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>. The PO<sub>4</sub> tetrahedron**

P	O10	O11	O12	O13
<b>O10</b>	<b>1.561(1)</b>	2.570	2.480	2.444
<b>O11</b>	113.82(12)	<b>1.506(2)</b>	2.501	2.485
<b>O12</b>	104.46(12)	108.56(12)	<b>1.576(2)</b>	2.526
<b>O13</b>	105.48(13)	114.10(12)	109.97(12)	<b>1.509(2)</b>

**The C<sub>3</sub>H<sub>6</sub>N<sub>3</sub>S<sub>2</sub> group**

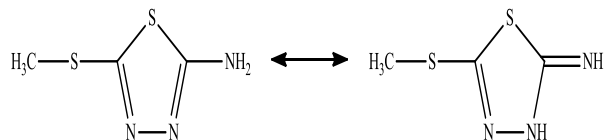
S1 - C2	1.744(3)	C2 - S1 - C8	101.18(14)
S1 - C8	1.806(3)	C2 - S3 - C4	87.68(14)
S3 - C2	1.753(3)	S1 - C2 - S3	118.94(17)
S3 - C4	1.743(3)	S1 - C2 - N6	125.1(2)
C2 - N6	1.286(4)	S3 - C2 - N6	116.0(2)
C4 - N5	1.331(4)	S3 - C4 - N5	109.7(2)
C4 - N7	1.312(4)	S3 - C4 - N7	123.7(2)
N5 - N6	1.385(6)	N5 - C4 - N7	126.6(3)
		C4 - N5 - N6	117.4(2)
		N5 - N6 - C2	109.2(2)

**Table 3. Hydrogen-bond geometry (Å, °) in [C<sub>3</sub>H<sub>6</sub>N<sub>3</sub>S<sub>2</sub>]<sub>2</sub>H<sub>2</sub>PO<sub>4</sub>.**

D-H...A	D-H(Å)	H...A(Å)	D-A(Å)	D-H...A(°)
N5-H51...O12 <sup>i</sup>	0.85	1.96	2.764(4)	158(1)
N7-H71...O13 <sup>ii</sup>	0.86	2.02	2.773(4)	147(1)
N7-H72...O11 <sup>iii</sup>	0.86	1.90	2.738(4)	163(1)
C8-H83...O12	0.95	1.56	3.447(4)	156
O10-H101...O11 <sup>iv</sup>	0.85	1.70	2.531(4)	167(1)
O12-H121...O13 <sup>v</sup>	0.82	1.71	2.515(4)	165(1)

Symmetry codes : (i) -x+2, -y+1, z-1/2; (ii) -x+1, -y+1, z+1/2; (iii) -x+3/2, y-1/2, z-1/2; (iv) x+1/2, -y+3/2, z; (v) x, y, z+1.

that the starting reagent exists as a mixture of the two following imine-enamine tautomers:



Consequently, the title compound is formed by action between the proton of the phosphoric acid and the exocyclic nitrogen atom of the imine form.

Refining the structure in the asymmetric space group gives a value of 0.64 (11) for the Flack parameter [9]. This value shows that the atomic arrangement corresponds to the correct absolute structure.

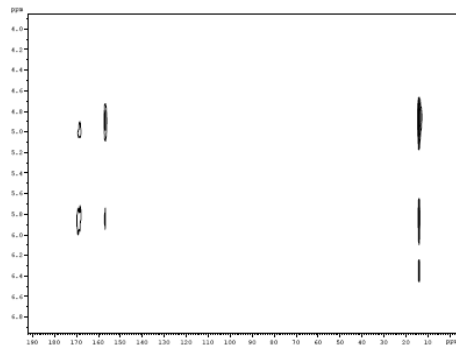


Fig. 7. Two-dimensional  $^{13}\text{C}$ -H CP-MAS-NMR spectrum of  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$ .

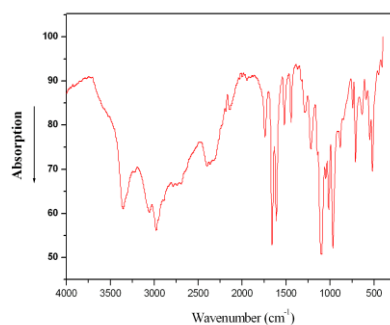
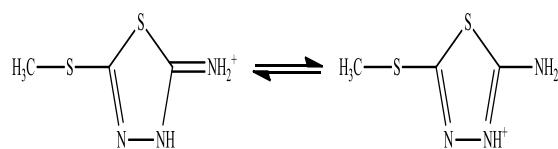


Fig. 8. IR spectrum of  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$ .

#### NMR spectroscopy

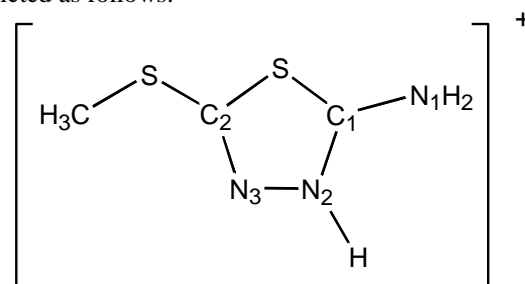
The  $^{15}\text{N}$  CP-MAS NMR spectrum of the title compound is shown on Figure 4. It displays 3 well-defined resonances, showing that the asymmetric unit cell should contain only one organic molecule. The solid state  $^{31}\text{P}$  MAS-NMR spectrum of the title compound is shown on Figure 5. The spectrum exhibits a single resonance peak at 0.9 ppm. This value agrees with those corresponding to monophosphate (between -10 and 5 ppm) [10-16] and is in agreement with only one phosphorus crystallographic site in the structure. The  $^{13}\text{C}$  CP-MAS NMR spectrum is shown on Figure 6. It displays four resonances. The splitting of the signal at 152 ppm proves that there are two very slightly different environments, probably due to the imine-enamine tautomerism:



The presence of such a mixture of two tautomeric forms in the same crystal has been already described in the literature [17, 18].

It is worth noting that the correlation peaks between the methyl protons and all the carbons in the  $^2\text{D}$   $^{13}\text{C}$ -1H spectrum (Figure 7) prove that all the peaks correspond to the same molecule.

Density functional theory (DFT) calculations were undertaken in order to assign the NMR resonances to the different crystallographically inequivalent carbon and nitrogen atoms of the unit cell. These calculations were made at the B3LYP/6-311++G\*\* level using the GAUSSIAN 09 program. Three different calculations were made on the organic cation and in all cases the theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane or glycine) calculated at the same level of theory: (i) calculation of the NMR chemical shifts (with the GIAO method) by taking the positions of atoms obtained by X-ray diffraction; (ii) optimization of the positions of the protons in the above molecule and calculation of the NMR chemical shifts in this semi-optimized geometry. Indeed X-ray diffraction leads always to underestimated X-H bond lengths, due to the fact that it is sensitive to the electronic cloud and does not see the nuclei; (iii) full optimization of all atoms and calculation of the corresponding NMR chemical shifts. This calculation, compared to the above one will give indications on the steric hindrance around the organic cation and on the positions where it is the strongest. Carbon and nitrogen atoms are depicted as follows:



The results, listed in Table 4, show that there is a relatively good agreement between the experimental and theoretical values calculated after optimization of the position of the protons, allowing unambiguously the attribution of the different NMR signals to the various carbon and nitrogen atoms of the structure.

#### IR spectroscopy

The IR spectrum of crystalline  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$  is shown in Figure 8. The most representative and characteristic vibrational modes of this compound can be compared to those of similar monophosphates [19]. In the high-frequency region, the very broad band, between 3600 and 2300  $\text{cm}^{-1}$ , corresponds to

Table 4. Calculated and experimental carbon-13 and nitrogen-15 chemical shifts for in  $[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$

Atom	X-ray (ppm)	Full optimization	Optimization of proton positions (ppm)	Experimental (ppm)
C1	180.1	178.4	176.6	156.9
C2	178.6	181.2	177.3	168.3 169.2
CH <sub>3</sub>	3.1	24.4	21.7	14.1
N1	74.1	95.8	95.2	83.5
N2	198.5	210.2	209.3	194.4
N3	322.3	323.5	325.2	293.6

the valence vibrations of C-H, N-H and O-H groups interconnected by a system of hydrogen bonds in the crystal [20]. Bands in the 1670 - 1200  $\text{cm}^{-1}$  region correspond to the bending vibrations of N-H and O-H groups and to the valence vibrations of C=N and C-C groups [21]. The observed bands in the range 1200 - 1000  $\text{cm}^{-1}$  can be attributed to the asymmetric stretching vibrations of the  $\text{PO}_4$  tetrahedra, and those in the 1000 - 800  $\text{cm}^{-1}$  region are related to the symmetrical ones [22]. The band at 1282  $\text{cm}^{-1}$  corresponds to the in-plane bending vibration  $\delta$  (P-O-H), while the out-of-plane bending vibration is observed at 710  $\text{cm}^{-1}$  [23]. The  $\text{PO}_4$  tetrahedra give also two asymmetric and symmetric bending vibration bands respectively observed in the frequency 700 - 500  $\text{cm}^{-1}$  and 500 - 300  $\text{cm}^{-1}$  ranges [24].

#### Supplementary material

Crystallographic data for the title compound have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC 872790). These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; mailto: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

#### Conclusion

$[\text{C}_3\text{H}_6\text{N}_3\text{S}_2]\text{H}_2\text{PO}_4$  was prepared as single crystals at room temperature and characterized by various physico-chemical methods. On the structural level, the framework of the title compound is built upon layers parallel to (0 1 0) made up from  $\text{H}_2\text{PO}_4^-$  entities associated by O---H...O strong hydrogen bonds. The organic cations are situated between the layers and connect them via N-H...O and C-H...O hydrogen bonding network. The exocyclic C-N bond length reveals the presence of the imine and enamine tautomers in the starting reagent. The numbers of solid state  $^{15}\text{N}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  CP-MAS-NMR peaks are consistent with only one organic cation in the asymmetric unit.

#### References

[1] R. Masse, M. Bagieu-Beucher, J. Pecaut, J.P. Levy, and J. Zyss, *J. Nonlin. Opt.* 5, 413 (1993).  
 [2] J. Zyss, in *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, J. L. Brédas and R. R. Chance, eds. (Kluwer, Dordrecht, *The Netherlands*, 1990), p. 545.

[3] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano; C. Giacovazzo, A. Guagliardi, A. Grazia, G. Moliterni, G. Polidori, and R. Spagna, *J. App. Cryst.* 32, 115 (1999).  
 [4] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, and D. J. Watkin, *J. Appl. Cryst.* 36, 1487 (2003).  
 [5] K. Brandenburg, Diamond Version 2.0 Impact GbR, Bonn., Germany, 1998.  
 [6] K. Kaabi, C. Ben Nasr and F. Lefebvre, *Mat. Res. Bull.*, 39, 205 (2004).  
 [7] A. Chtioui and A. Jouini, *Mat. Res. Bull.*, 41, 569 (2005).  
 [8] A. Chtioui, I. Benhamde and A. Jouini, *Mat. Res. Bull.*, 40, 2243 (2005).  
 [9] H. D. Flack, *Acta Cryst.* A39, 876 (1983).  
 [10] P. Hartmann, J. Vogel, and B. Schnabel, *J. Magn. Reson.* 111, 110 (1994).  
 [11] K. Kaabi, A. Rayes, C. Ben Nasr, M. Rzaigui, and F. Lefebvre, *Mater. Res. Bull.* 38, 741 (2003).  
 [12] A. Oueslati, A. Touati, C. Ben Nasr, and F. Lefebvre, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 181, 2117 (2006).  
 [13] R. Kefi, A. Rayes, C. Ben Nasr, and M. Rzaigui, *Mat. Res. Bull.*, 42, 404 (2006).  
 [14] J. Oueslati, A. Oueslati, C. Ben Nasr, and F. Lefebvre, *Solid State Sci.*, 8, 1067 (2006).  
 [15] M. L. Mrad, C. Ben Nasr, and M. Rzaigui, *Mat. Res. Bull.*, 41, 1287 (2006).  
 [16] R. Kefi, C. Ben Nasr, and F. Lefebvre, *Cryst. Res. Technol.*, 42, 333 (2007).  
 [17] V. Gerhardt, M. Tutughamiarso, M. Bolte, *Acta Cryst.* C67, o179 (2011).  
 [18] C. Lopez, R.M. Claramunt, I. Alkorta, and J. Elguero, *Spectroscopy* 14, 121 (2000).  
 [19] M. Charfi, and A. Jouini, *J. Solid. Chem.* 127, 9 (1996).  
 [20] I. Nemeč, I. Cisarova, and Z. J. Micka, *J. Solid State Chem.* 140, 71 (1998).  
 [21] S. M. Haile, P.M. Calkins, and D. Boysen, *J. Solid State Chem.*, 139, 373 (1998).  
 [22] R. Kefi, C. Ben Nasr, and F. Lefebvre, *Cryst. Res. Technol.*, 42, 333 (2007).  
 [23] H. Naïli, T. Mhiri, and A. Daoud, *Int. J. Inorg. Mater.*, 3, 393 (2001).  
 [24] B. Stuart, *Modern Infrared Spectroscopy*, Wiley, England (1996).