

Characterization of a new organic-cation dihydrogenmonoarsenate: [C₄H₁₂N]H₂AsO₄

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ABSTRACT : Physicochemical properties of an organic dihydrogenmonoarsenate are discussed on the basis of its X-ray crystal structure investigation. [C₄H₁₂N]H₂AsO₄, denoted tBAs, crystallizes in the monoclinic system with P2₁/c space group. Its unit cell dimensions are a = 14.2655(7), b = 6.3265(2), c = 17.9401(7) Å, β = 147.261(2)° with V = 875.63(6) Å³ and Z = 4. The structure has been solved using direct method and refined to a reliability R factor of 0.039 for 1447 reflections. The compound is characterized by infinite [H₂AsO₄]_n²ⁿ⁻ chains, parallel to the b direction, connected by organic cations and forming layers localized at x = 1/2. The cohesion of the framework is ensured by hydrogen bonds N(O)-H...O. Thermal behavior exhibits an irreversible phase transition. IR bands are attributed by comparison with spectra of similar other compounds.

Keywords : Organic dihydrogenmonoarsenate, Chemical preparation, Crystal structure, Thermal behavior, Infrared spectroscopy.

RÉSUMÉ : Les propriétés physico-chimiques d'un dihydrogénomonoarséniate organique sont discutées en se basant sur l'investigation structurale. [C₄H₁₂N]H₂AsO₄, noté tBAs, cristallise dans le système monoclinique avec un groupe d'espace P2₁/c. Les dimensions de sa maille sont a = 14.2655(7), b = 6.3265(2), c = 17.9401(7) Å, β = 147.261(2)° avec V = 875.63(6) Å³ et Z = 4. La structure a été résolue en utilisant la méthode directe et affinée jusqu'à R = 0.039 pour 1447 réflexions. Le composé est caractérisé par des chaînes infinies [H₂AsO₄]_n²ⁿ⁻, parallèles à la direction b, elles sont connectées par des cations organiques formant des plans localisés à x = 1/2. La cohésion de ce réseau est assurée par les liaisons hydrogènes N(O)-H...O. L'analyse thermique par ATG -ATD et DSC montre une transition de phase irréversible d'enthalpie 17.96 kJ/mol. L'étude spectroscopique IR permet les attributions des bandes du spectre IR aux différents types de mouvements atomiques au sein du tBAs.

Mots clés : Dihydrogénomonoarséniate organique, Préparation chimique, Structure cristalline, Comportement thermique, Spectroscopie IR.

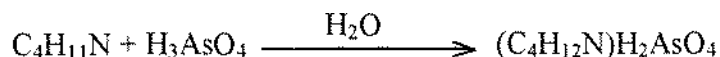
I- INTRODUCTION

The crystal chemistry of alkyl cations encapsulated between chains of [HXO₄]_n²ⁿ⁻ or [H₂XO₄]_nⁿ⁻ (X = P, As) polyanions is fascinating because it may lead to single crystals of polar materials. Such a crystal engineering route combines the cohesion and flexibility of anionic inorganic lattices with the enhanced polarizability of organic entities [1]. Beside non-linear optical properties [2], some arsenates exhibit phase transitions, like (C₆H₁₆N)[H₂AsO₄] and (C₈H₂₀N)[H₂AsO₄] [3]. The present study is part of a systematic investigation of the interaction of various arsenic acids with amines. This study allowed the finding of a new organic arsenate, (C₄H₁₂N)H₂AsO₄, whose chemical preparation, crystal structure, thermal behavior and IR spectrum are discussed.

II- CRYSTAL CHEMISTRY

The present compound was prepared by adding dropwise 0.04 mol of *tert*-butylamine in water to 400 mL of a solution containing 0.04 mol arsenic acid. During this operation the solution was stirred vigorously. The synthesis reaction is:

* correspondant



When most of the solution is evaporated, cubic crystals with square section, appear deep down the vessel.

III- CRYSTAL DATA AND STRUCTURE DETERMINATION

A colorless crystal with 0.40 x 0.25 x 0.35 mm dimensions was selected for the structure determination. The data were collected on a Nonius Kappa-CCD diffractometer using monochromated $K\alpha(\text{Mo})$ radiation with a specimen-to-image plate distance of 2.7 cm; 90 frames were recorded, each being of 2° in ϕ and 120 s. The first ten frames were used for indexing reflections using the *DENZO* package and refined to obtain the final cell parameters. A total of 6335 reflections had their intensities integrated and scaled, yielding finally to 1447 independent reflections [4]. The reflections were corrected for Lorentz and polarization; no absorption correction was performed. Preliminary photographs indicated a monoclinic symmetry and system atically absent reflections of the $P2_1/c$ space group.

The crystal structure solution carried out with direct method permitted location of the AsO_4 group. The other non-hydrogen atoms were rapidly located after subsequent cycles of refinement and difference-Fourier syntheses using the program SHELXL-97 [5]. Anisotropic factors were only attributed to As, O, C and N atoms; the least-squares refinement, including isotropic hydrogen atoms leads to the final reliability factors $R = 0.039$ ($R_w = 0.093$). The average density, $D_m = 1.60(3) \text{ g cm}^{-3}$, measured at room temperature using toluene as pycnometric liquid, is in agreement with the calculated $D_c = 1.63 \text{ g cm}^{-3}$. Table I reports the crystallographic characteristics and the experimental conditions of data collection and refinement. The final atomic coordinates are given in table II.

IV- STRUCTURE DESCRIPTION

It is well known that As–OH distances are, in general, longer than As–O distances [6], and that As–OH distances increase as the strength of the hydrogen bond, $\text{O} \cdots \text{H} \cdots \text{O}$ increases, that is, as $\text{O} \cdots \text{O}$ decreases. Moreover, it is also rather well-established that in response to increases in As–OH bond lengths, the remaining As–O bonds of an AsO_4 group tend to shorten. Decreases in the $\text{O}_A \cdots \text{O}_D$ distance are also accompanied by a decrease in the difference between the $\text{H} \cdots \text{O}_D$ and $\text{H} \cdots \text{O}_A$ distances, and there is a tendency for very strong hydrogen bonds to be symmetric (where O_D and O_A are donor and acceptor oxygen atoms, respectively, in the $\text{O}_D \cdots \text{H} \cdots \text{O}_A$ bond) [7]. In our investigation of the structure of tBAs use of correlations between As–OH, As–O, and $\text{O} \cdots \text{O}$ distances proved a powerful tool for identifying donor and acceptor oxygen atoms.

Two types of As–O distances are observed in AsO_4 tetrahedra depending on whether O atoms are hydrogen donors (1.709–1.707 Å) or acceptors (1.642–1.667 Å). As expected, the As–OH distances are significantly longer than the other As–O distances. Consequently, it is possible to use differences in bond lengths to identify which O in the $\text{N}(\text{O})\text{--H} \cdots \text{O}$ bonds is more highly associated. O(1) and O(4) with As–O bond distances of 1.642(2) and 1.667(3) Å, participate in two hydrogen bonds, meanwhile As–O(1) is shorter than As–O(4). This is due to the fact, that O(4) is involved in hydrogen bonds stronger than those with O(1). The high sensitivity of bond distances to the strength and the number of the hydrogen bonds which may be formed has also been noted in other crystal structures including similar entities such as sulfates and monophosphates [8–10]. The calculated values of the distortion indices [11], in the H_2AsO_4 tetrahedra [$\text{DI}(\text{AsO}) = 0.0159$, $\text{DI}(\text{OAsO}) = 0.030$, $\text{DI}(\text{OO}) = 0.0133$], exhibit a pronounced distortion of OAsO angles if compared to AsO and OO distances. These indices are in accordance with the overall mean values obtained for H_nAsO_4 ($n = 1, 2$) which indicate that $\text{DI}(\text{OAsO}) \approx 2\text{DI}(\text{AsO}) \approx 2\text{DI}(\text{OO})$ [12].



TABLE I: Main crystallographic features. x-ray diffraction data and results of tBAs

I. Crystal data	
Formula: $(C_4H_{12}N)H_2AsO_4$	$F_w = 215.08$ g/mol
Crystal system: Monoclinic	Space group: $P2_1/c$
$a = 14.2655(7)$ Å, $b = 6.3265(2)$ Å,	$V = 875.63(6)$ Å ³
$c = 17.9401(7)$ Å, $\beta = 147.26(7)^\circ$	$Z = 4$
$\rho_{calcd} = 1.63$, $\rho_{measd} = 1.60(3)$ g.cm ⁻¹	$F(000) = 110$
Linear absorption factor	$\mu(MoK\alpha) = 0.962$ mm ⁻¹
Morphology	cube
Crystal size	0.40x0.25x0.35
II. Intensity measurements	
Diffraction measurement device	Kappa CCD Nonius
Monochromator:	Graphite plate
Wave length: (MoK α)	0.7107 Å
Computing data collection	Kappa CCD Nonius
Computing cell refinement	Kappa CCD Nonius
Computing data reduction	Denzo [4]
θ range and temperature:	2.87-26.32° ; 298 K
h_{min} ; k_{min} ; l_{min} :	-17 ; 0 ; -22
h_{max} ; k_{max} ; l_{max} :	17 ; 7 ; 16
Number of scanned reflection:	6335
III. Structure determination	
Computing structure solution	SHELXS-97 [5]
Computing structure refinement	SHELXL-97 [5]
Reflections number observed	1447
Reflections observed criterion	2 sigma(I)
Refined parameters/ S	148/1.196
Extinction Coefficient	0.352(13) [5]
R_w/R	0.0934/0.0395
Weight: $W=1/[\sigma^2(F_o^2)+(0.0268P)^2+1.3922P]$	where $P=(F_o^2+2F_c^2)/3$

The $H_2AsO_4^-$ groups exhibit a compact assembly of oxygen atoms in which the arsenic atom shows a slight displacement from the center of gravity of the tetrahedra; this displacement doesn't exceed 0.0837 Å. The anionic arrangement can be described as linear chains, made up from $H_2AsO_4^-$ anions, running along the **b** axis and interconnected via O–H...O strong hydrogen bonds ($d_{O...O} < 2.73$ Å) [13] (Figure 1). The two arsenate anions involved in the hydrogen bonds system are located around the inversion center at (1/2, 1/2, 0). The O...O distances involved in the hydrogen bonds [2.572(3) and 2.680(3) Å] are of the same order of magnitude as in the $H_2AsO_4^-$ acidic tetrahedron [2.684(3)–2.793(3) Å]. The short distance As–As (4.267 Å) between successive arsenic atoms in the chain and the strength of the O–H...O hydrogen bonds, allows as considering the $[H_2AsO_4]_n^{n-}$ as a polyanion.

The only crystallographically independent cation $NH_3^+C(CH_3)_3$, present in this atomic arrangement has no internal symmetry. The geometrical features measured in *tert*-Butylammonium are similar to intramolecular bond distances and angles usually reported for such species [14, 15].


TABLE II: Final atomic coordinates and U_{eq} (U_{iso} for H atoms) of tBAs

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
As	0.47508(4)	0.74817(3)	0.40353(3)	0.0273(2)
O(1)	0.5355(3)	0.6475(3)	0.3637(2)	0.0412(6)
O(2)	0.2888(3)	0.6326(4)	0.3106(2)	0.0474(6)
O(3)	0.4162(3)	1.0037(3)	0.3470(2)	0.0397(5)
O(4)	0.6245(3)	0.7394(2)	0.5706(3)	0.0351(6)
N	0.6268(4)	0.2440(4)	0.3805(3)	0.0320(6)
C(1)	0.8208(4)	0.2033(5)	0.5099(3)	0.0367(7)
C(2)	0.8473(6)	- 0.0156(7)	0.4954(5)	0.059(1)
C(3)	0.8825(7)	0.219(1)	0.6301(5)	0.069(1)
C(4)	0.9024(6)	0.3697(7)	0.5147(6)	0.064(1)
H(1N)	0.570(5)	0.145(6)	0.372(4)	0.037(9)*
H(2N)	0.603(5)	0.383(6)	0.380(4)	0.044(9)*
H(3N)	0.573(5)	0.232(5)	0.300(5)	0.04(1)*
H(1C2)	0.963(6)	- 0.055(7)	0.571(5)	0.07(1)*
H(2C2)	0.800(6)	- 0.122(8)	0.491(5)	0.08(1)*
H(3C2)	0.803(6)	- 0.015(8)	0.407(5)	0.1(2)*
H(1C3)	0.988(9)	0.196(9)	0.704(7)	0.09(2)*
H(2C3)	0.837(9)	0.10(1)	0.632(7)	0.13(2)*
H(3C3)	0.87(1)	0.35(1)	0.642(9)	0.13(3)*
H(1C4)	1.026(7)	0.333(9)	0.597(5)	0.08(1)*
H(2C4)	0.873(6)	0.505(8)	0.520(5)	0.07(1)*
H(3C4)	0.845(8)	0.36(1)	0.423(7)	0.11(2)*
H(O2)	0.316(5)	0.513(8)	0.348(4)	0.071(1)*
H(O3)	0.390(6)	1.086(7)	0.368(4)	0.07(1)*

Note. Starred atoms were refined isotropically. Esds are given in parentheses. $U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

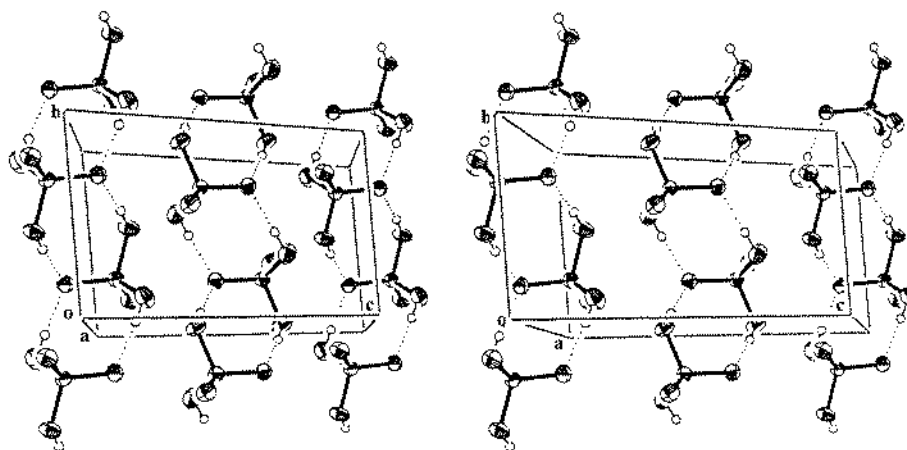


Figure 1: ORTEP Stereoscopic projection of the anionic arrangement. (H-bonds are represented by dashed lines). Thermal ellipsoids are given at 50% probability.

The interatomic bond lengths and angles spread within the respective ranges: 1.498(6)–1.520(4) Å and 106.87(3)–112.3(4)° (table III). The organic cations $[(CH_3)_3CNH_3]^+$ are located between chains. Each organic group simultaneously links two adjacent chains in the **b** and **c** directions to establish the infinite layer (figure 2). Stability between successive layers is performed

by van der Waals interactions originating from the organic cations. Such interaction was recently observed in the organic monohydrogenphosphite $(\text{H}_3\text{NC}_4\text{H}_9)(\text{HPO}_3\text{H})$ [16].

The determined bonding angles in the NH_3^+ group spread in the range $103(3)$ – $112(3)^\circ$. The reason why the expected tetrahedral symmetry of these groups is somewhat disturbed probably lies in the intense participation of the protons in the hydrogen bond system of the $\text{N-H}\cdots\text{O}$ type [17].

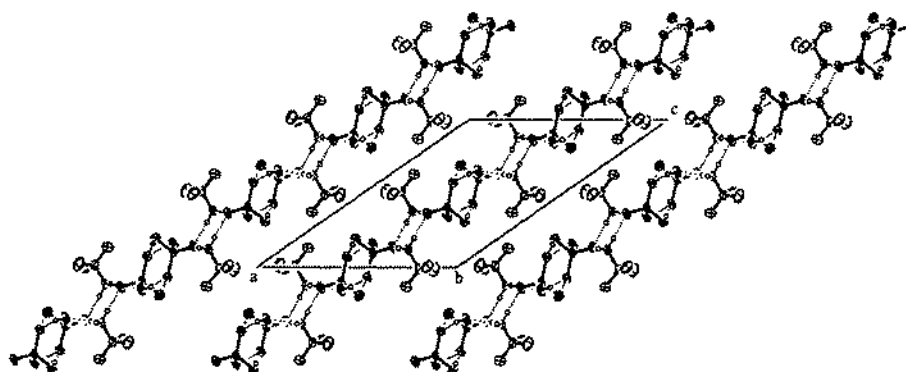


Figure 2. ORTEP projection of the atomic arrangement along the *b* axis (For clarity, the H atoms of Carbon are omitted; H-bonds are represented by dashed lines). Thermal ellipsoids are scaled to enclose 50% probability.

TABLE III: Main inter atomic distances (Å) and bonds angles ($^\circ$) in the tBAs.

AsO ₄ tetrahedron				
As	O(1)	O(2)	O(3)	O(4)
O(1)	<u>1.642(2)</u>	111.4(1)	106.5(1)	115.1(1)
O(2)	2.769(3)	<u>1.709(2)</u>	104.0(1)	109.1(1)
O(3)	2.684(3)	2.692(3)	<u>1.707(2)</u>	110.2(1)
O(4)	2.793(3)	2.751(3)	2.769(3)	<u>1.667(3)</u>
Organic group				
C(1)–C(2): 1.498(6)		C(2)–C(1)–C(3): 112.3(4)		
C(1)–C(3): 1.514(5)		C(2)–C(1)–C(4): 110.8(4)		
C(1)–C(4): 1.517(5)		C(2)–C(1)–N : 106.8(3)		
C(1)–N : 1.520(4)		C(3)–C(1)–C(4): 112.2(4)		
		C(3)–C(1)–N : 107.3(3)		
		C(4)–C(1)–N : 107.1(3)		

Figure 3 shows an ORTEP [18], projection of the crystal packing. Each arsenate anion is surrounded by seven hydrogen bonds: acceptor for three NH_3 and two neighboring H_2AsO_4 and donor to two neighboring H_2AsO_4 . Each anion is bridged to three different cations and two $\text{H}_2\text{AsO}_4^{2-}$ anions with $\text{N}(\text{O})\cdots\text{O}$ distances ranging from 2.572(3) to 2.942(3) Å. The hydrogen bonds $[\text{N}(\text{O})\text{–H}\cdots\text{O}]$ range from 1.70(5) to 2.04(4) Å in length ($\text{H}\cdots\text{O}$) with $\text{N}(\text{O})\text{–H}\cdots\text{O}$ angles from $163(3)$ to $179(6)^\circ$ (table IV). The structure contains five donors [O(2), O(3) and 3 NH_3] and three acceptors [O(1), O(3) and O(4)].


TABLE IV: Bond lengths(Å) and angles(°) in the hydrogen-bonding scheme in tBAs

	N(O)–H	H···O	N(O)···O	N(O)–H···O
N–H(1N)···O(3 ^a)	0.92(4)	2.04(4)	2.942(3)	163(3)
N–H(2N)···O(1)	0.94(4)	1.83(4)	2.765(3)	175(4)
N–H(3N)···O(1 ^b)	0.90(5)	1.92(5)	2.804(4)	169(3)
O(3)–H(O3)···O(4 ^c)	0.86(5)	1.70(5)	2.572(3)	170(4)
O(2)–H(O2)···O(4 ^d)	0.88(5)	1.82(5)	2.680(3)	179(6)

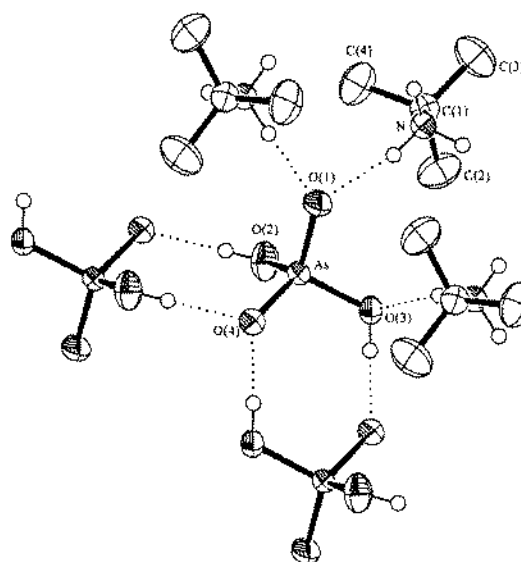
Note.

a)x, y-1, z

b)-x+1, y-0.5, -z+0.5

c)-x+1, -y+2, -z+1

d)-x+1, -y+1, -z+1

Figure 3. ORTEP view of the atomic arrangement (For clarity, the H atoms of Carbon are omitted; H-bonds are represented by dashed lines). Thermal ellipsoids are given at 50% probability.


V- THERMAL BEHAVIOR

From the TG-DTA thermograms (Figure 4), we deduce that the anhydrous compound decomposes in the range 195-350°C, with evolution of ammonia represented by a set of endotherms at 225 and 254°C [19]. Within this temperature range, a rather bad smell escapes from the resulting black compound. The DTA curve shows a weak endothermic peak occurring in the temperature range 134-151°C. This peak may be ascribed to a phase transition with a ΔH of 17.96 kJ/mol, calculated from the DSC curve (Figure 5a). To study the reversibility of the transformation by thermal analysis, 11 mg of the sample are placed in an aluminum crucible, heated from 25°C to 180°C and cooled to the ambient temperature (Figure 5b). The thermal phenomenon absence during cooling, confirms the irreversibility of the phase transition. Slight differences between temperatures of peaks obtained in DSC and ATD thermograms, is due to the difference between sensibilities of the two equipments and to the taken masses in ATD and DSC. The decomposition occurring with melting is confirmed by an additional thermal treatment in a separate carbolite furnace with run heating of 3°C/min from room temperature to 255°C, the resulting compound being a black liquid.

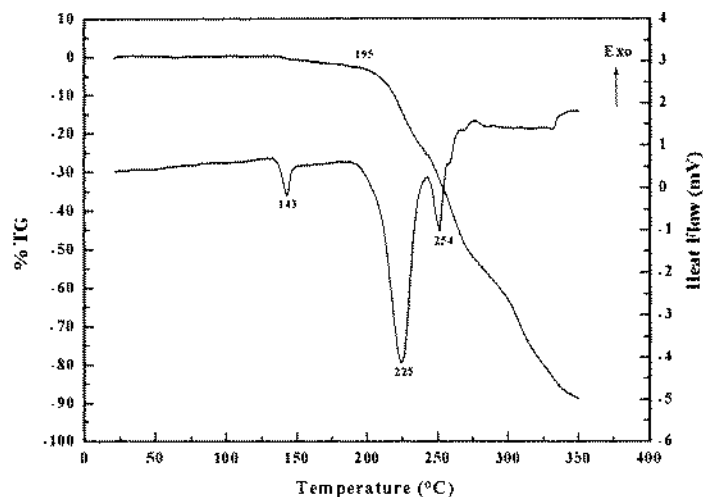


Figure 4: TG-DTA thermogram of tBAs.

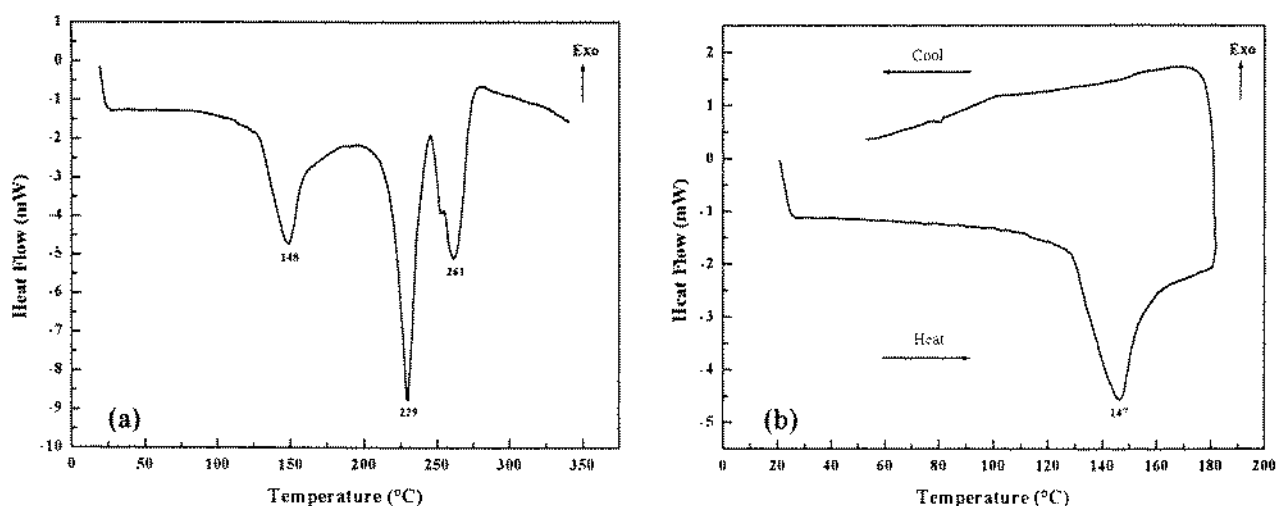


Figure 5. DSC thermograms: (a) heat trace, (b) heat and cool trace.

VI- IR SPECTROSCOPIC INVESTIGATION

To make a qualitative assignment of IR peaks to vibrational modes, we examine the modes and frequencies observed for H_2AsO_4^- anion [20,21]. The ideal, five atoms AsO_4 tetrahedral group exhibit T_d symmetry. Thus, there are nine vibrational modes, only four of which are independent: $\nu_1(A_1) = \text{AsO}_4$ symmetric stretch, $\nu_2(E) = \text{O-As-O}$ bend, $\nu_3(T_2) = \text{AsO}_4$ asymmetric stretch and $\nu_4(T_2) = \text{O-As-O}$ bend. The average frequencies observed for these modes are: $\nu_1 = 837 \text{ cm}^{-1}$, $\nu_2 = 349 \text{ cm}^{-1}$, $\nu_3 = 878 \text{ cm}^{-1}$ and $\nu_4 = 463 \text{ cm}^{-1}$ [22]; among these modes only ν_3 and ν_4 are IR active. The influence of the addition of two protons to the anion can be understood through a two-step process. First, in H_2AsO_4 , two of the oxygen atoms are replaced with two hydroxyl groups with points mass. This reduces the symmetry from T_d to C_{2v} , and eliminates degeneracies such that there are nine rather than four independent vibrational modes. Second, the vibrations associated with the hydroxyl group are considered. There should be six symmetric or asymmetric modes: O-H stretching, As-O-H in-plane bending and As-O-H out-of-plane bending (or torsion) [20]. The two stretching vibrations, asymmetric and symmetric of AsO_2 group, are observed respectively at 1036 and 988 cm^{-1} , while those related to As(OH)_2 occur as two intense bands at 866 and 760 cm^{-1} . The splitting of T_2 stretching mode of AsO_4 , into three intense components at 1036 , 988 and 866 cm^{-1} corroborates the symmetry lowering of H_2AsO_4 in the solid state; it is to be noted that H_2AsO_4



observed in this structure exhibit no internal symmetry. On the other hand, bending modes of H_2AsO_4 group are observed at lower frequencies. The two medium bands at 380 and 347 cm^{-1} , correspond respectively to the torsion $\tau(\text{AsO}_2)$ and to the bending $\delta(\text{O-As-O})$ vibrations. The two mediums at 456 and 447 cm^{-1} , and the shoulder one at 401 cm^{-1} correspond respectively to rocking $\rho(\text{AsO}_2)$, wagging $\omega(\text{AsO}_2)$ and to the bending $\delta(\text{OHAsOH})$ vibrations. Bands at 1298 and 1214 cm^{-1} are attributed to in-plane bending $\delta(\text{As-O-H})$, the out-of-plane bending vibrations $\gamma(\text{As-O-H})$ are observed as two weak bands at 670 and 656 cm^{-1} . The weak band at 2074 cm^{-1} and the shoulder one at 1733 cm^{-1} , correspond respectively to the O-H stretching modes of H_2AsO_4^- anion.

The remaining observed bands in the spectrum can be assigned to CH_3 , NH_3^+ and skeletal symmetric and asymmetric stretching and deformation modes. The domain of high frequencies in the spectrum is characterized by N(C,O)-H stretching, combination bands and harmonics, while the lower one corresponds to the bending and to the external modes. The IR spectrum of tBAs is depicted in Figure 6. The NH_3 and CH_3 symmetric and asymmetric stretching modes are observed in the range $3206\text{--}2486\text{ cm}^{-1}$. The "indicator band" at 2032 cm^{-1} in the IR spectrum is an important indication of the presence of NH_3^+ in the compound. This band is a combination of the asymmetric deformation vibration and torsion vibration of the NH_3^+ group [23]. Frequencies in the range $1717\text{--}1503\text{ cm}^{-1}$ are attributed to N-H bending mode. The shifting of the stretching and bending vibrations of the NH_3 group from the free state value confirms the formation of hydrogen bonds of varying strengths in the crystal. CH_3 bending, wagging and rocking may occur in the range $1477\text{--}1375\text{ cm}^{-1}$.

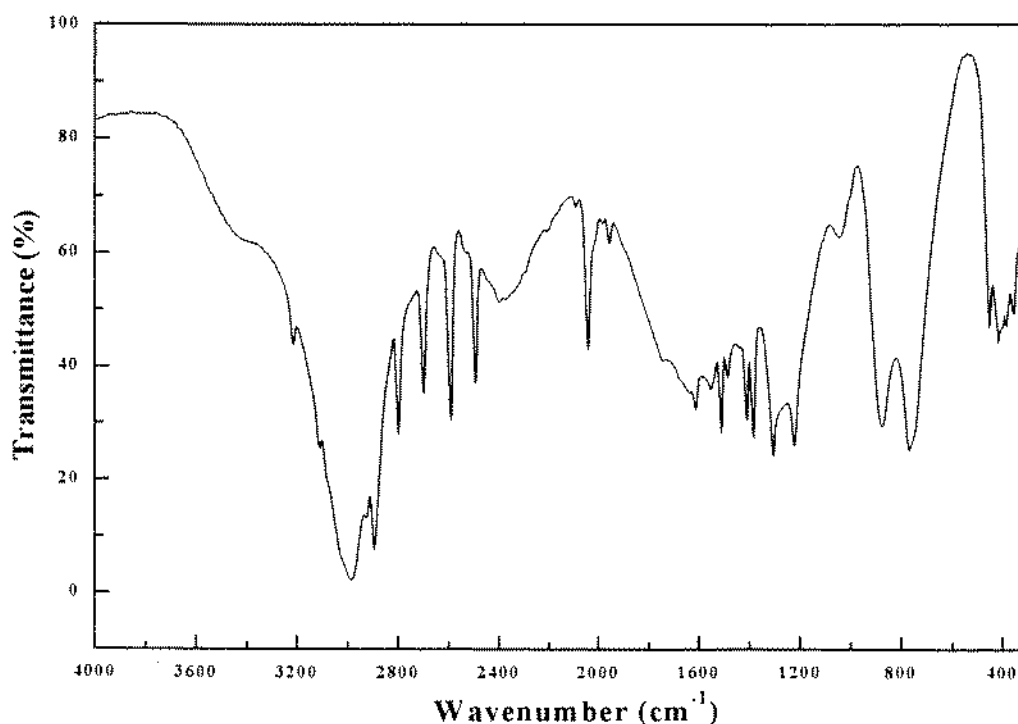


Figure 6: IR spectrum of tBAs in polycrystalline form.

VII- CONCLUSION

Crystals of tBAs have been prepared by slow evaporation, at room temperature, of aqueous solution of H_3AsO_4 and tert-butylamine. Organic cations are anchored to the anionic arrangement, by hydrogen bonds $\text{N-H}\cdots\text{O}$ forming infinite layer parallel to the b direction. Stability between successive layers is performed by van der Waals interactions originating from the organic cations.



The thermal behavior study exhibits an irreversible phase transition in the anhydrous compound tBAs. IR spectrometric investigation, supported by group theoretical analysis allows the attribution of bands to the different atomic motions.

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