

THE HYBRID COMPOUNDS AND THE INFLUENCE OF HYDROGEN BONDING

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Abstract

Organic–inorganic hybrid materials have received increasing attention in recent research particularly because of their ability to combine the specific properties of inorganic frameworks and the features of organic molecules, including the formation of weak interactions. These materials have recently attracted further interest due to their attractive potential for application as insulators in the electronics industry. They offer promising opportunities for the development of efficient conductors, ferroelectrics, and semiconductors in a wide range of electronic applications [1,2]. The hybrid compounds are rich in H-bonds and they could be used to this effect because of their potential importance in constructing sophisticated assemblies from discrete ionic or molecular building blocks due to its strength and directionality. In order to enrich the varieties in such kinds of hybrid materials and to investigate the influence of hydrogen bonds on the on the structural features, they have synthesized a new compound, This kind of hydrogen bonding appears in the active sites of several biological systems and is observed in similar previously studied hybrid compounds.

Keywords: diffraction of RX, hybrid compounds, hydrogen bond.

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I. INTRODUCTION

This work is part of our research on intermolecular interactions in hydrogen-bonded molecular and ionic crystals. In recent years investigations of hybrid materials have attracted a great deal of attention; in addition to their interesting structural topologies and potential application in the field of new materials science, such as ion-exchange, adsorption, molecular recognition, catalysis and magnetism, hybrid compounds have very interesting electrical, magnetic and optical properties. The kind of hydrogen bonding in hybrid compounds is also present in the active sites of several biological systems.

The hybrid compounds are rich in H-bonds and they could be used to this effect because of their potential importance in constructing sophisticated assemblies from discrete ionic or molecular building blocks due to its strength and directionality. The combination of the organic matrix and the mineral anions allowed us to obtain original structures.

We were able to isolate two new compounds:

- o-Carboxyanilinium dihydrogen phosphate (o-CADP)

Acta Cryst. E63, o2054–o2056, (2007).

- o-Carboxyanilinium dihydrogen phosphite (o-CADPx)

Acta Cryst. E65, o664–o665, (2009).

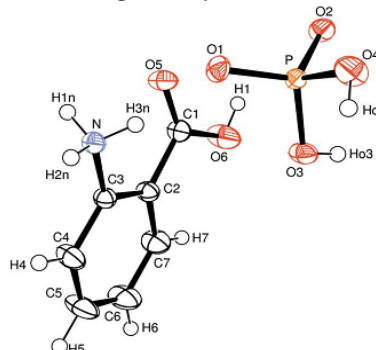
II. RESULTS AND DISCUSSION

A-HYDROGEN BONDING IN 2-CARBOXYANILINIUM DIHYDROGEN PHOSPHATE (O-CADP):

The structure of the title compound, $C_7H_8NO_2^+$, $H_2PO_4^-$, shows that a single proton transfer occurs. The anions and cations are held together via strong and short O—HO hydrogen bonds, in addition to N—H O interactions. The three-dimensional complex network of hydrogen bonds ensures the cohesion of the ionic structure.

The structure (I) (Fig. 1), is composed of cationic $HOO-C_6H_4-NH_3^+$ and anionic $H_2PO_4^-$ layers alternating along the *a* axis with a spacing of 5.239 (3) Å.

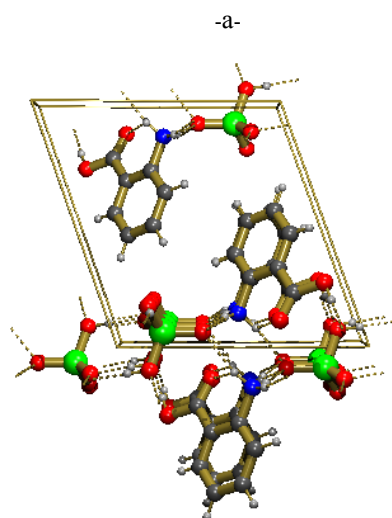
Fig.1. the asymmetric unit.



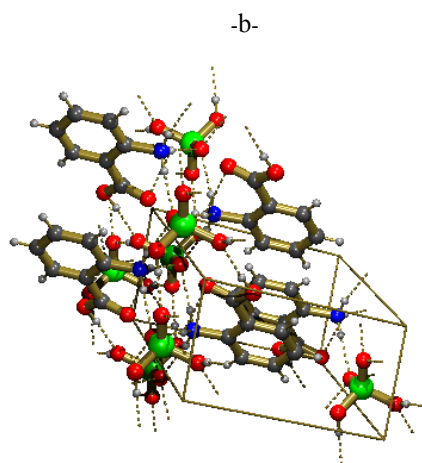
A unit-cell projection down the *a* axis, showing the hydrogen-bonding (dashed lines) network and the alternating layers of $C_7H_8NO_2^+$ and $H_2PO_4^-$.

There are two types of hydrogen bonds that are observed in (I): cation–anion and anion–anion interactions. Each of the cations is bonded to the anions via hydrogen bonds as shown in Fig. 2 (a-b) The protonated N atoms are involved in the strongest hydrogen bonds via intermolecular interactions to Phosphate. Another strong interaction involving the carboxylic acid group is observed between anions and cations. The crystal packing is established by the arrangement of parallel layers Fig.3. of anions and cations.

Fig 2: A unit-cell projection down the a axis, showing the hydrogen-bonding



(dashed lines) network and the alternating layers of $C_7H_8NO_2^+$ and $H_2PO_4^-$



The table 1 showing the different hydrogen bonding in the structure.

D: Donneur H: Hydrogène et A: Accepteur.

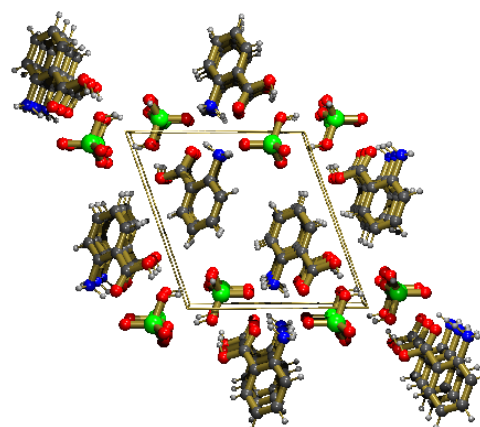


Fig.3. The arrangement of parallel layers of anions and cations.

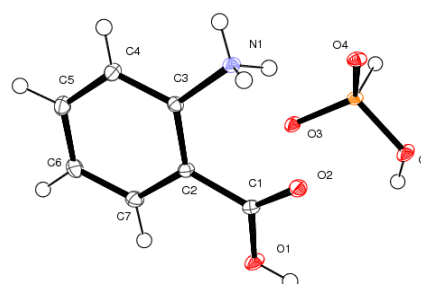
Table 1: The hydrogen bond of (o-CADPX).

D—H...A	D—H (Å°)	H...A (Å°)	D...A (Å°)	D—H...A (°)
N-H3N...O1	0,89	1,98	2,856(2)	166,7
N-H2N...O1	0,89	2,01	2,8880(10)	170,3
N-H1N...O1	0,89	1,97	2,852(2)	172,8
O3-HO3...O2	0,82	1,77	2,584(10)	173,1
O4-HO4...O2	0,82	1,78	2,564(2)	159,1
O6-H1...O3	0,82	1,98	2,794(2)	173,6
C6-H6...O2	0,93	2,67	3,399(2)	135,3
C7-H7...O6	0,93	2,44	2,759(2)	100,0

B- HYDROGEN BONDING IN 2-CARBOXYANILINIUM DIHYDROGEN PHOSPHITE (O-CADPX):

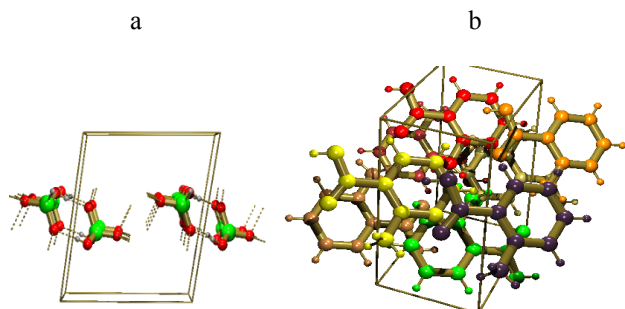
The structure (I) (Fig. 4), is composed of cationic $HOO-C_6H_4-NH_3^+$ and anionic $H_2PO_3^-$

Fig 4. ORTEP of the asymmetric unit of the $COOH - C_6H_4 - NH_3^+ \cdot H_2PO_3^-$.



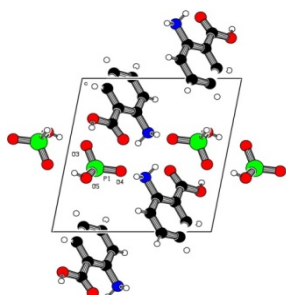
The title compound, $C_7H_8NO_2^+ \cdot H_2PO_3^-$, is formed from alternating layers of organic cations and inorganic anions stacked along the a- (Figure 5). They are associated via O—HO, N—HO and C—HO hydrogen bonding, giving rise to two different $R_2^2(8)$ graph-set motifs and generating a three-dimensional network.

Fig 5. Alternating layers of organic cations –b- and inorganic anions-a-



The organic cations are placed between dimères (figure 6) $[(H_4P_2O_6)]^{2-}$ formed by the grouping of $H_2PO_3^-$

Fig 6.the dimeres of anionic group.



The three H atoms of the anilinium group are subsequently involved in extensive N—H...O hydrogen-bonding (table 2) interactions with O4 being a multiple acceptor of three different phosphate anions, while O3 behaves as double acceptor of hydrogen bonds from one cation, via O1 in the carboxylic group, and one anion, via O5 in the phosphite anion. These interactions give raise to two different $R_2^2(8)$ graph set motifs (Bernstein et al. 1995), shown in Fig 7. In addition, there are intramolecular interactions involving the benzene ring and the carboxylic group ensuring cohesion and stability of the crystal structure.

Fig.7. the cohesion of the structure by hydrogen bonds.

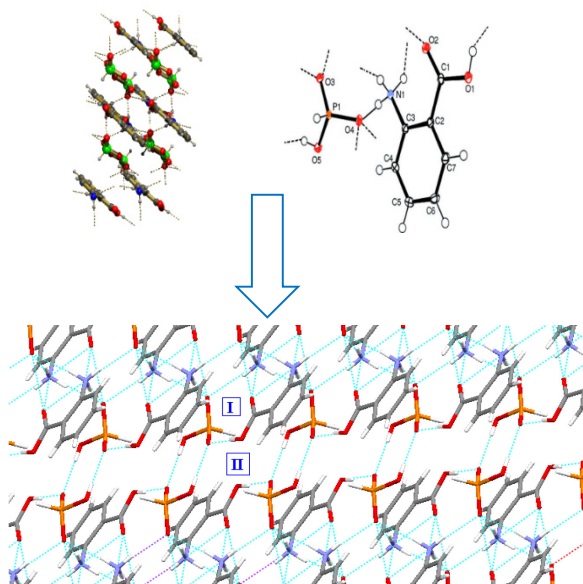


Table 2 : The hydrogen bonding

D—H...A	D—H (Å°)	H...A (Å°)	D...A (Å°)	D—H...A (°)
O1-H1...O3 ⁱ	0,84	1,77	2,6085(13)	178
N1-H1A...O4	0,91	1,96	2,8589(14)	169
N1-H1B...O4 ⁱⁱ	0,91	2,02	2,9160(13)	169
N1-H1C...O4 ⁱⁱⁱ	0,91	1,97	2,8740(14)	173
O5-H5O...O3 ^{iv}	0,84	1,78	2,6059(13)	167
O6-H6...O5	0,95	2,55	2,8542(15)	132

III. COMPARAISON :

To determine the influence of hydrogen bonds in our structure we made a comparison study between the two hybrid compounds o-CADP and o-CADPx, the network of hydrogen bond shows that there are six hydrogen bonds in o-CADP and eight in o-CADPx and also many difference in the length and angles distances between the cations of the two structure (table 3-4) and all this difference it's due to the cohesion of the structures by strong hydrogen bond O—H...O and N—H...O and weak bonds C—H...O.

Table 3: the distances (Å°) in the two cations COOH-C₆H₄-NH₃⁺

Atom (1)	Distance(Å°) <i>o-CADP</i>	Distance(Å°) <i>o-CADPx</i>
C1-O5	1,203(2)	1,2186(14)
C1-O6	1,3230(10)	1,3247(13)
C1-C2	1,4903(18)	1,4924(15)
C2-C3	1,3977(18)	1,4056(15)
C3-C4	1,3830(19)	1,3884(15)
C4-C5	1,389(2)	1,3970(16)
C5-C6	1,378(3)	1,3898(17)
C6-C7	1,385(2)	1,3919(16)
C7-C2	1,395(2)	1,3976(15)
Average distance C- C: 1.3879 (8)		
1.39505 (15) for the ring		

The difference between this distance it's due to the protonation of the organic which appear a numbers of interaction (hydrogen bond) which linked the cation with the anion. we observe that in the first coumpound o-CADP there are two hydrogen bond between O6-H...O2 and O3 where as in o-CADPx there is only one hydrogen bond O6-H...O5, and three N-H...O1, this bonds have a big influence in the difference values of length between the two compounds

Table 4: the angles (°) in the cation $\text{COOH-C}_6\text{H}_4\text{-NH}_3^+$

Atom (1-2-3)	Angle (°) o-CADP	Angle (°) o-CADPx
O6-C1-O5	122,62(13)	123,18(10)
O5-C1-C2	123,48(12)	122,43(10)
O6- C1-C2	113,87(12)	114,35(10)
C1- C2-C3	120,80(12)	121,50(10)
C1- C2-C7	120,66(12)	120,28(10)
N- C3-C2	121,52(11)	121,43(9)
N- C3-C4	117,74(12)	117,67(10)
C3- C2-C7	118,49(13)	118,17(10)
C2- C3-C4	120,72(13)	120,89(10)
C3- C4-C5	119,77(14)	119,91(10)
C4- C5-C6	120,28(14)	119,99(10)
C5- C6-C7	119,96(15)	119,74(11)
C6-C7-C2	120,78(14)	121,27(11)
Average Angle C-C-C : 120(14) for th ring.		

The distortion of the angles it's due also to the hydrogen bond. The table 4 show that there are difference in angles between the two cations and exactly in the NH_3 and COOH .

we can see that the two compounds have the same geometrical characteristics in both structures.

o-CADP	o-CADPx
a = 4,8541(8) Å.	a = 4,876 Å.
b = 9,9845(9) Å.	b = 9,460 Å.
c = 10,4849(2) Å.	c = 10,080 Å.
$\alpha = 108,383(5)^\circ$.	$\alpha = 78,93^\circ$.
$\beta = 97,816(8)^\circ$.	$\beta = 76,06^\circ$.
$\gamma = 96,816(6)^\circ$.	$\gamma = 86,81^\circ$.
Z = 2,	Z = 2,
Triclinique : P-1.	Triclinique : P-1.
V/Z = 235,87	V/Z = 221,4

Finally, the o-CADP and CADPx two isostructural compounds are a perspective and crystal packing interactions, their parameters are different, but they have similarities:

- The two salts crystallize in the group of P-1 space triclinic system.

- Both structures consist of alternating layers of H_2PO_3^- anionic and cationic H_2PO_4^- , $\text{C}_6\text{H}_4 - \text{COOH} - \text{NH}_3^+$.

- The cohesion of the crystal is ensured by intra and intermolecular hydrogen bonds types $\text{OH} \dots \text{O}$ and $\text{NH} \dots \text{O}$. Intermolecular interactions by hydrogen bonds between the cations and anions are similar in the (o-CADP) and (o-CADPx) Indeed, H_2PO_3^- anion H_2PO_4^- and acceptor are the three hydrogens of the ammonium groups form bonds hydrogen with three different oxygen anions.

- In (o-CADPx), the interconnection between H_2PO_3^- groups is effected by a strong hydrogen bond length $\text{O5} \dots \text{O3}$ 2.606

(1) Å to form dimers $[(\text{H}_4\text{P}_2\text{O}_6)]^{2-}$. While in the o-CADP, H_2PO_4^- the groups are bonded on the one hand by a strong hydrogen bonding $\text{O2} \dots \text{O3}$ length 2.284 (2) Å between two molecules to form dimers $[(\text{H}_4\text{P}_2\text{O}_8)]^{2-}$, and secondly by another hydrogen bond ($\text{O4} \dots \text{O2} = 2.564$ (2) Å) to form chains along the axis **a**. In conclusion, both complexes have The cation $\text{C}_6\text{H}_4 - \text{COOH} - \text{NH}_3^+$ has the same geometrical characteristics in both complexes. As for the inorganic anions, they present two different arrangements. The same types of hydrogen bonds ensure the cohesion between the cations and anions in the two salts.

IV. CONCLUSIONS

The crystal structure of compound o-Carboxyanilinium dihydrogenphosphite (o-CADPx) $\text{C}_7\text{H}_{10}\text{NO}_5\text{P}$ is constructed based on an asymmetric unit consists of a o-Carboxyanilinium cation $\text{C}_6\text{H}_4 - \text{COOH} - \text{NH}_3^+$ and a dihydrogenphosphite H_2PO_3^- anion. The development in the three directions of space, led to cationic and anionic plans.

The junction between these planes is carried out by strong hydrogen bonds, medium and low. Both strong bonds of $\text{OH} \dots \text{O}$ are established between the anions and cations of carboxyl groups. The distances and angles relating to the three links $\text{NH} \dots \text{O}$ formed between anions and cations, prove protonation of the ammonium group. For binding Alternative hydrogen lowest, interatomic $\text{CH} \dots \text{O}$, is observed from hydrogen H_7 benzene ring and O_1 oxygen atom of carboxyl group.

The combination of the organic matrix and anions minerals allowed us to obtain original structures [I, II]. Presenting connections hydrogen strong, average or low (weak). Actually, several crystals of this type were isolated in our laboratory.

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