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Transfer Of Protons Into A New Organic Compound Based On Creatinine †

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Abstract: Hydrogen bonds are of paramount importance for biological processes, they are energetically weaker than covalent bonds, and their cumulative effect strengthens the three-dimensional shape of macromolecules and maintains their structure. The weakness of these bonds is responsible for the flexibility and conformational dynamics that are necessary for the flexibility of biomolecules, which gives them their recognition capacity and therefore their very high specificity.

New compounds have been obtained by proton transfer reactions between organic compounds of type nitrogenous substance and dicarboxylic acid. These reactions present interesting aspects for the realization of molecular systems whose properties can be monitored by X-ray diffraction.

In recent literature there are many examples of organic molecules functionalized with hydrogen bond donor-acceptor groups. Carboxylic acids are a few examples which illustrate excellent model systems for the preparation of new compounds with proton transfer, hence our interest in studying new organic compounds based on creatinine and organic acids which form complexes with many organic molecules

In this study, we shed light on the structural study of a new proton transfer compound. In this crystal structure, creatinine is protonated by two hydrogens of fumaric acid, forming a new organic compound, Bis Creatinium fumarate fumaric acid, that is rich in strong hydrogen bonds.

Keywords: Proton transfer, single crystal, X-ray diffraction, H-bonds

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1. Introduction

Creatinine (2-amino-1,5-dihydro-1-methyl-4H-imidazol-4-one) is an organic biomolecule used in the synthesis of some charge transfer organic compounds [1], these organic compounds have also a predominant role in a wide range of chemical and biochemical processes such as solvation, catalytic, enzymatic reactions [2,3], and acid-base neutralization [4]. Although the development of creatininium salts continues to grow and a considerable number of research groups have gained great interest,a search in the Cambridge Structural Database CSD (ConQuest Version 2021.2) [5] for crustal structures containing creatininium molecules results in 26hits, 24 of them crystallize in a centro symmetric space group.

2. Experimental

2.1. Synthesis of Bis creatininium fumarate fumaric acid(BCFF)

The single crystals of (**BCFF**) were obtained by slow evaporation of a mixture of two aqueous solutions, Creatinine and fumaric acid, according to the following reaction:

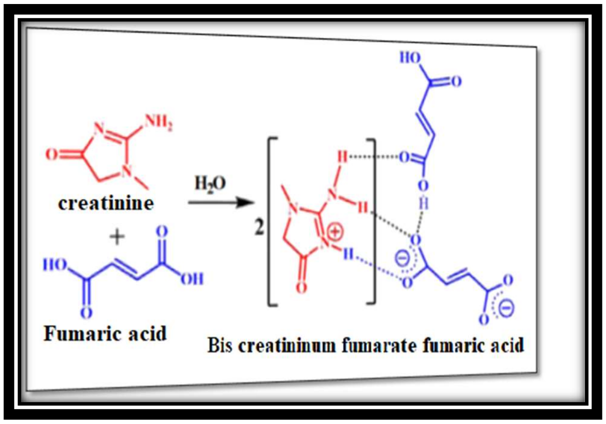


Figure 1. Synthesis reaction of the compound BCFF.

Single crystals were obtained after a few weeks, by slow evaporation at room temperature.

Figure 2. Single crystals of the (BCFF).

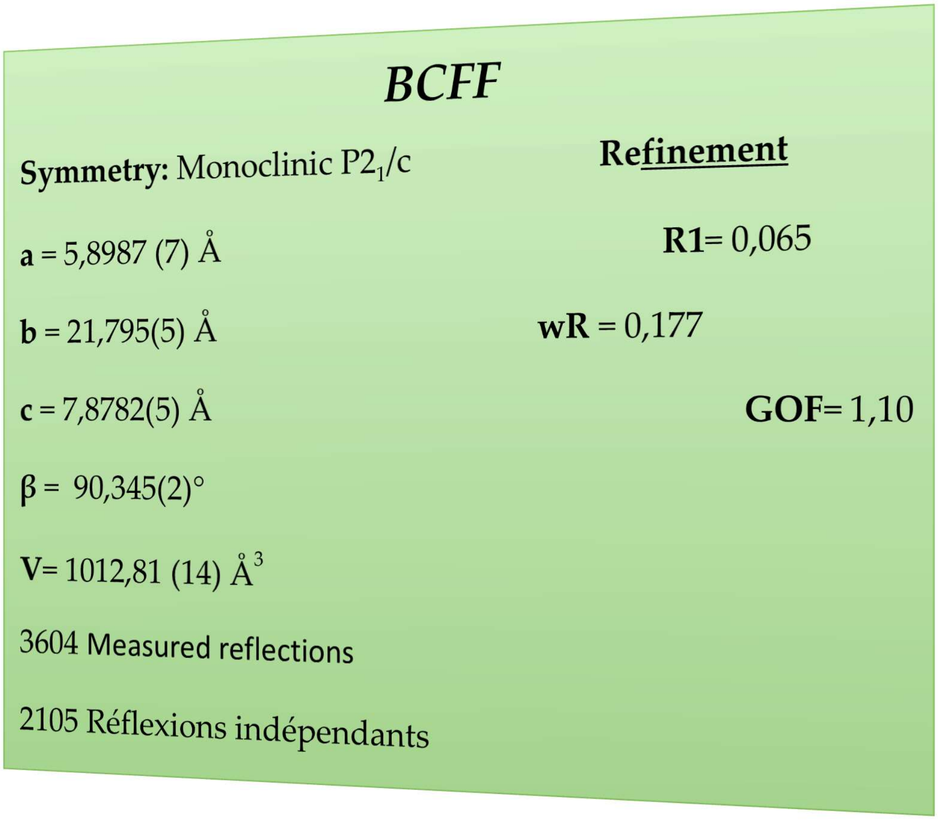
3. Cristallographic study

3.1. Resolution Structural and Refinement Of the tructure

The refinement of the lattice parameters and the data collection of a transparent prismatic crystal, of dimension (0.75 x 0.51 x 0.27 mm), was carried out on a Gemini Oxford diffractometer equipped with an associated CCD detector [6], with Kα radiation of molybdenum (λ = 0.71073 Å).

The crystallographic data and the recording conditions are given in the following table.

Table 1. Main crystallographic data and structure refinement for compound (BCFF).



BCFF

Symmetry: Monoclinic $P2_1/c$

Refinement

a = 5,8987 (7) Å

R1= 0,065

b = 21,795(5) Å

wR = 0,177

c = 7,8782(5) Å

GOF= 1,10

β = 90,345(2)°

V= 1012,81 (14) Å^3

3604 Measured reflections

2105 Réflexions indépendants

X-ray diffraction and resolution with adequate software shows that the compound crystallizes in a monoclinic crystal systems with a centro-symmetric space group ($P2_1$ / c).

The reliability factors R and WR reveal the good quality of the refinement.

The large number of reflections and the quality of the data allo wed us to make a good structural resolution [7].

3.2. Discussion of Structure

The asymmetric unit of (BCFF) consists of a creatinium cation (A), half of a fumarate anion (B) and half of a neutral molecule of fumaric acid (C).

the creatinium cation is monoprotonated at the level of the imino group N1.

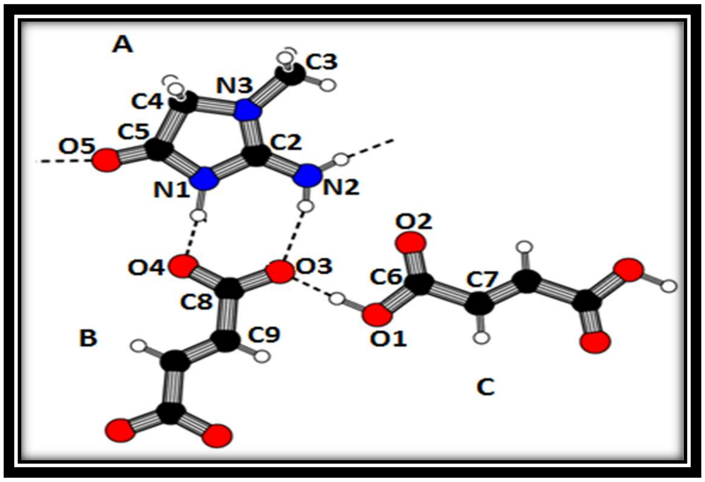


Figure 3. View of the ionic structure of (BCFF), showing the immediate hydrogen-bonded between creatininium, fumarate and fumaric acid.

The crystalline stacking of (BCFF) is built by alternating planes developing along the axis b, the plane of cations A to b = 1/4 and b = 3/4 and the plane B / C is located at b = 0 and b = 1/2 is a mixture between the molecules of fumaric acid and fumarate anion, so that the molecules are perpendicular to each other.

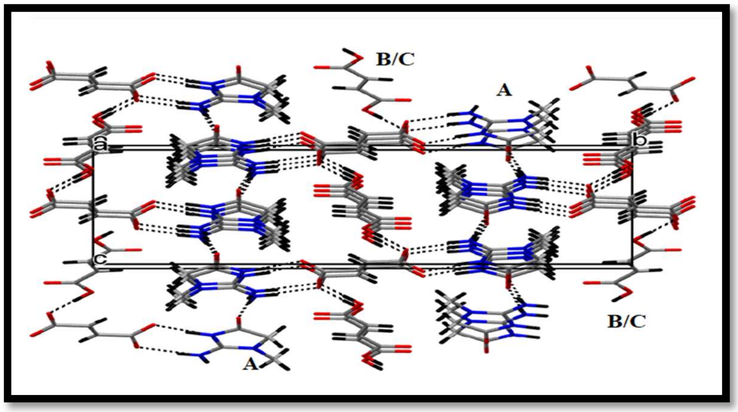
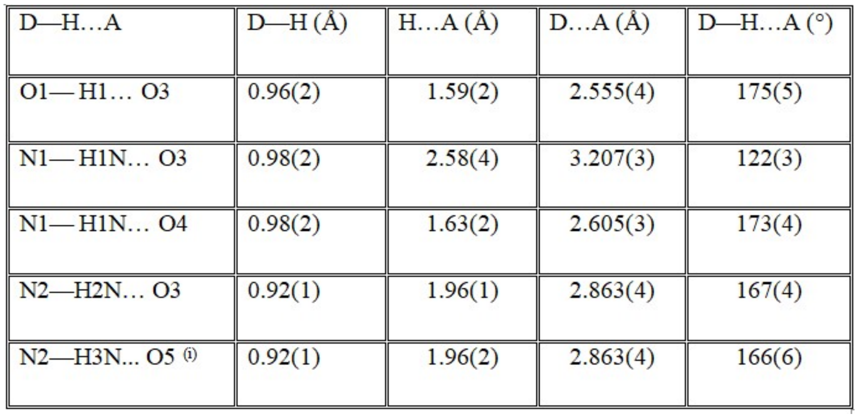


Figure 4. packing of the BCFF unit-cell.

The characteristic hydrogen bonds of this compound are reported in the following Table :

Table 2. Hydrogen bond lengths (Å) and angles (º).(BCFF).



D—H…A	D—H (Å)	H…A (Å)	D…A (Å)	D—H…A (°)
O1— H1… O3	0.96(2)	1.59(2)	2.555(4)	175(5)
N1— H1N… O3	0.98(2)	2.58(4)	3.207(3)	122(3)
N1— H1N… O4	0.98(2)	1.63(2)	2.605(3)	173(4)
N2—H2N… O3	0.92(1)	1.96(1)	2.863(4)	167(4)
N2—H3N... O5 (i)	0.92(1)	1.96(2)	2.863(4)	166(6)

Scheme 1. −*y*+1/2, *z*+1/2.

4. Conclusion

The crystal structure of the compound Bis Creatininum fumarate fumaric acid crystallizes in the P21 / C space group of the monoclinic system, is built on the basis of an asymmetric unit consisting of two Creatininium cations **2 $(C_4H_8N_3O)^+$**the fumarate ion **$(C_4H_2O_4)$** $^{-2}$ and a fumaric acid molecule **$C_4H_4O_4$.**

Intermolecular cohesion is ensured by a network of hydrogen bonds of the (O-H… O), (N-H… O) type between the organic cation creatinium, the fumarate anion and fumaric acid.

The crystalline edifice, allowed us to determine their binary graphs, formed mainly by finite and infinite cycles and chains, as well as the higher order graphs between several types of bonds.

5. References

[1] V. Thayanithi, P. Praveen Kumar, B. Gunasekaran, IUCrData 1, 2016, p. x160989.

[2] T.L. Wang, H.K. Chiang, H.H. Lu, F.Y. Peng, Opt. Quant. Electron. 37 (2005) 1415e1422.

[3] N.M. Settergren, P. Buhlmann, E.A. Amin, J. Mol. Struct. Theochem. 861 (2008) 68e73.

[4] M. Nagasaka, H. Kondoh, K. Amemiya, T. Ohta, Y. Iwasawa, Proton transfer in waterehydroxyl mixed overlayers on Pt (111): combined approach of laser desorption and spatially-resolved X-ray photoelectron spectroscopy, Surf. Sci. 603 (10) (2009) 1690e1695.

[5] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, Acta Crystallogr. B 72 (2016) 171e179.

[6] CrysAlisPro, Oxford Diffraction Ltd, version 1.171.34.40 (rel. 2021, CrysAlis171. NET).

[7] W. Falek, R. Benali-Cherif, L. Golea, S. Samai, N. Benali-Cherif, El. Bendeif, I. Daoud, J. Mol. Struct, 1192 (**2019**) 132-144.