

To compare the strengths of these interactions and to investigate their geometrical preferences, the approach suggested by Lommerse et al. [1], using the normalized distance R_{HX} and the spatially normalized distance vs. angle (R_{HX}^3 vs. $1 - \cos[180 - (D-H \cdots X)]$) plot, was applied.

The study implies: (1) Even if the N-H(s) were deprotonated / substituted, O-H(s) and C-H(s) in the molecules could serve as hydrogen bond donors. O-H(s) are normally better donors than N-H(s), while C-H(s) build weaker interactions. (2) No notable differences were found among F, Cl and Br in both examined criteria. (3) In general, the capability as hydrogen bond acceptor is $X^- > X-M > X-C$, which is complied with results of others [2]. (4) Important counter anions in coordination chemistry, such as BF_4^- , PF_6^- and SbF_6^- , exhibit comparable hydrogen bond acceptor capabilities like transition metal-halides. (5) Special attention is drawn to MX_4^{2-} type counter anions (templates). The several cases recorded show exclusively the formation of much stronger hydrogen bonds compared to normal metal-halides. Their possible roles in complex synthesis and nucleation are still unclear, further studies with theoretical methods would follow. (6) Although CH_2Cl_2 / $CHCl_3$ are often used and are observed in structures, X-C is seldom involved in hydrogen bonding. In the rare cases at most very weak interactions were built. While on the other hand the increased acidity of the C-H(s) makes them possible hydrogen bond donors.

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Keywords: hydrogen bond, halogens, N-heterocycles

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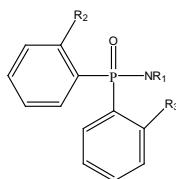
Structural investigation of phenol-phosphonic amides

C.Alicia Renison, D.Bradley.G Williams, Alfred.J Muller and Stephen.J Evans, *Research Centre for Synthesis and Catalysis, Department of Chemistry, University of Johannesburg, Auckland park, Johannesburg 2006, (South Africa)*. E-mail: aliciarenison@yahoo.com

The synthesis and use of phosphine ligands in homogeneous catalysed reactions is a field of research that is gaining more interest [1]. There is currently a special focus [2] on the synthesis of unsymmetrical ligands, for various reasons, including asymmetric catalytic transformations [3]. The stereoelectronic nature of the ligand plays a significant role in the outcome of the reaction² and, as a result, we have investigated a potentially new route to ortho-substituted arylphosphine ligands.

Several of these ligands are crystalline which enables their investigation by means of X-ray crystallography. A series of phenol-phosphonic amides was investigated as shown in Scheme 1. An interesting feature exhibited by all of these structures is that of phenol-phosphine oxide intramolecular hydrogen bonding. Packing motifs, hydrogen bonding and geometrical features of the structures were compared in this study.

Calculation of Tolman cone angles and solid angles were determined to illustrate the steric behaviour of these phosphine ligands [4]. Electrostatic potential properties such as V_{min} and d_{cp} were calculated in order to quantify the electronic effect of these ligands. The calculations were performed in Gaussian with Density functional theory (DFT) incorporating the B3LYP functional and 6-31G(d,p) basis set [5].



$R_1 = Et, Pr, Bu, R_2 = H, OH, R_3 = H, OH, PPh_2$

Scheme 1: Phenol phosphonic amides

[1] P.W.N.M. Leeuwen, P.C.J. van Kamer, J.N.H. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741-2770. [2] W. Tang, X. Zhang, *Chem. Rev.* **2003**, *103*, 3029-3069. [3] S. Jeulin, S.D. de Paule, V. Ratovelomanana-Vidal, J.P. Genêt, N. Champion, P. Dellis, *Angew. Chem. Int. Ed.* **2004**, *43*, 320-325. [4] C.A. Tolman, *Chem. Rev.* **1977**, *77*, 313-348. [5] C.H. Suresh, N. Koga, *Inorg. Chem.* **2002**, *41*, 1573-1578.

Keywords: phosphonic-amides, hydrogen-bonding, DFT

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How many molecules can you crystallize in one experiment? the role of hydrogen bonding in chalcone-flavanone isomerization.

Miriam Rossi,^a Michelle Duong,^a Francesco Caruso,^b ^a*Department of Chemistry, Vassar College, Poughkeepsie, NY 12604 (USA)*. ^b*CNR, Istituto di Chimica Biomolecolare, c/o Università "La Sapienza", Roma, Piazzale Aldo Moro 5, 00185 Roma (Italy)*. E-mail: rossi@vassar.edu.

Chalcones, flavones and flavanones are naturally occurring compounds from plants and they have a wide range of biological activities. We are interested in studying the molecular structures using X-ray diffraction of these compounds so that a relationship between the chemical structure and the biological activities may be seen. The crystallization of $C_{16}H_{14}O_5$, 3-methoxy-4,2',5'-trihydroxyxchalcone from a mixture of ethanol-water produced *three* different types of crystals which were visually distinct. We report the results of these 3 crystal structure determinations that show, respectively, the chalcone and the flavanone isomers and a third structure showing the conformational disorder resulting from the molecular rearrangement due to the intramolecular isomerization reaction between the flavanone and the chalcone molecular structure! The role that intermolecular interactions such as hydrogen bonding and stacking play in the self assembly and biological activity of these structures is investigated.

Keywords: chalcone, flavanone, molecular rearrangement

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The hydrogen bond in supramolecular network

Marcos Flores-Alamo, Ana Laura Maldonado-Hermenegildo, Humberto Gómez-Ruiz, *Unidad de Servicios de Apoyo a la Investigación, Facultad de Química, Universidad Nacional Autónoma de México, (México D.F.) 04510*. E-mail: mfa@unam.mx

In recent years, supramolecular arrangement and intermolecular interactions have played an important role in crystal engineering. A detailed analysis of hydrogen bonds in some molecules can classify this as *I- very strong*, *II- strong* and *III-weak* [1]. An easy way to visualize the intermolecular interactions is to apply a graphical analysis of the patterns that represent these interactions [*motif* $G_d^a(r)$] [2] in crystals. In this paper we analyze the crystals of the organic substance enrofloxacin and other inorganic substances such as copper acetate, ferrous sulfate, etc. Of X-ray data, tables are constructed of lengths and hydrogen bond angles. Finally we illustrate how to classify the bond and its possible application in Crystal Engineering and / or the design of molecular devices. Below is a brief summary of this work.

Data collection X-ray diffractometer was carried out with a Gemini with Atlas area detector and two sources of radiation λ_{Mo} = 0.7103 and λ_{Cu} = 1.5418 Å to 130 K.

The asymmetric unit of enrofloxacin corresponds to the moiety

formula $C_{19}H_{22}FN_3O_3 \cdot 6(H_2O)$ which crystallizes in a triclinic crystal system with space group $P-1$. Water molecules of the network array of hydrogen bonding interactions of the type O-H...H with distances that are within the range of 1.93 a 2.23 Å and as a few examples, in this case shows that some water molecules have three hydrogen bonds at the same time, which favors a two-dimensional crystal growth with the *motif* $R^6_6(12)$, giving rise to the supramolecular arrangement in a lamina.

In the dimeric complex of copper acetate (II) with molecular formula $C_8H_{16}Cu_2O_{10}$, have a monoclinic crystal system with space group $C2/c$, in this compound the water molecules establish three hydrogen bonds in the range of 2.03 to 2.58 Å, giving rise to *motif* $R^2_2(8)$ mainly. While for crystals of $[Fe(H_2O)_6]SO_4 \cdot 2(H_2O)$ (II) with molecular formula $FeH_{12}O_6 \cdot 2(SO_4) \cdot 2(H_2O)$ crystallizing in a monoclinic crystal system with space group $P2_1/n$; the large number of water molecules present in this complex supports a large number of such interactions O-H...H with hydrogen bond lengths are in the range of 1.85 to 2.19 Å.

In a global analysis of data from X-ray diffraction, is that the magnitude of the hydrogen bonds are present in the energy range of 4 to 15 Kcal, being strong bonds with weak covalence and dominant electrostatic contribution, these properties are required for the design and application engineering of crystals and / or molecular devices

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Keywords: hydrogen-bond, motif, engineering-crystals

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Structural analysis of aziridine-2-methanol derivatives

Aurelia Falcicchio,^a Angela Altomare,^a Corrado Cuocci,^a Renzo Luisi,^b Anna Moliterni,^a Rosanna Rizzi,^a ^a*Istituto di Cristallografia IC-CNR, Via Amendola 122/o 70126 Bari (Italy).* ^b*Dipartimento Farmaco – Chimico, Università degli Studi di Bari “Aldo Moro”, Consorzio C.I.N.M.P.I.S., Via E. Orabona 4, Bari (Italy).* E-mail: aurelia.falcicchio@ic.cnr.it

Aziridines are widely used as versatile building blocks for the synthesis of a variety of biologically and pharmaceutically important molecules [1]. Among the available methodologies for the preparation of functionalised aziridines, the lithiation/trapping sequence of simple parent aziridines is growing in importance [2]. Present work reports the results concerning the structural study of aziridine-2-methanol derivatives by dynamic nuclear magnetic resonance (DMNR) [3] and single crystal X-ray diffraction. A careful examination of the aziridine 2 (see figure 1) by NMR data, shows that at room temperature the meta protons and the protons of the two ortho methyl groups of the mesityl ring gives featureless lumps, likely as consequence of a restricted rotation around the Csp^3-Csp^2 bond between the carbinolic carbon and the ipso carbon of the mesityl ring. Also in the solid state, an almost identical arrangement of the mesityl ring, with respect to the other two phenyl rings, has been observed. In this case, the aziridine nitrogen substituent was found in a syn relationship with respect to the carbinolic group so preventing the possibility of forming a hydrogen bond with the hydroxyl group. This evidence underlines a slow rotation of the mesityl group instead of a nitrogen inversion as usually is expected. By X-ray analysis of 3 and *diast-3* (figure 1), it is estimated that the nitrogen substituents set on the opposite side with respect the carbinolic carbon. *Via* study of crystal structures, the presence of hydrogen bonds between the hydroxyl group and the aziridine nitrogen lone pair was ascertained for aziridine 3 but not for *diast-3* (figure 1). Such

a hydrogen bond, which is persistent also in solution, could prevent the formation of conformational diastereoisomers by rotation around the bond between the carbinolic carbon and the aziridine quaternary carbon. This hypothesis has been demonstrated by

NMR experiments. This investigation allowed us to calculate some Csp^2-Csp^3 and Csp^3-Csp^3 rotational barriers and highlight a sort of “geared” rotation between aryl and alkyl substituents; this is possible if the structure is not in a locked conformation by an hydrogen bond as demonstrated by NMR and X-ray diffraction.

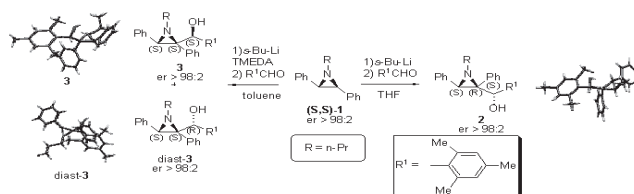


Figure 1

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Proton migration in molecular complexes of urea and its derivatives

Andrew O. F. Jones,^{a,b} L. H. Thomas,^c G. J. McIntyre,^d C. C. Wilson,^c ^a*Department of Chemistry, University of Glasgow, Glasgow (UK).* ^b*Institut Laue-Langevin, Grenoble (France).* ^c*Department of Chemistry, University of Bath, Bath (UK).* ^d*Bragg Institute, ANSTO, Sydney (Australia).* E-mail: anjone@chem.gla.ac.uk

Systems showing proton disorder, transfer and migration are an area of much interest in recent times with widespread implications for areas such as ferroelectrics and enzyme action. These often subtle processes can affect the properties of systems and are often observed in materials containing short strong hydrogen bonds. They can be probed using variable temperature diffraction experiments. We aim to identify and characterise systems that show such effects, with a view to predicting and controlling this potentially “tunable” behaviour. These processes have previously been observed in complexes of urea [1].

Single crystal X-ray and neutron diffraction have been used to study molecular complexes of urea and its derivatives with a particular focus on characterising the hydrogen atom behaviour. The proton behaviour is monitored over variable temperatures, with the aim of observing movement of the proton with changing temperature. A limited number of such mobile proton effects have been observed using variable temperature diffraction measurements, and this project aims to build on these observations by extending these investigations to further, related, systems. The instrument used for the neutron studies is the single crystal Laue diffractometer VIVALDI at the ILL in Grenoble which is ideal for use here due to its potential for high throughput single crystal diffraction of small samples.

Temperature dependent proton migration in the 2:1 complex of N,N-dimethylurea and oxalic acid has been observed by single crystal X-ray and neutron diffraction data confirming the existence of this phenomenon. Accurate determination of the hydrogen atom parameters in this system is vital in understanding this phenomenon and also in explaining a single-crystal to single-crystal phase transition