

FA4-MS33-P19

Triphenylguanidine Salts: Hydrogen bonding and NLO Properties. Pedro S. Pereira Silva^a, Manuela Ramos Silva^a, José A. Paixão^a, Ana Matos Beja^a^aCEMDRX, Physics Department, University of Coimbra, PortugalE-mail: psidonio@pollux.fis.uc.pt

The calculation of the nonlinear optical (NLO) properties of solids using structural data has been stimulated by the increasing importance of the communications industry and the parallel need for materials having suitable properties. Classical molecular requirements for second-order NLO effects are strongly elongated and conjugated molecules, asymmetricized by interacting donor and acceptor groups. Although they often exhibit extremely large hyperpolarizabilities, some major drawbacks are associated with their dipolar character, e.g. a high tendency towards unfavourable aggregation and small off-diagonal tensor components. It was recognized that octupolar molecules can circumvent the aforementioned disadvantages, since these nonpolar molecules combine excellent (second-order) NLO characteristics with a strict cancellation of all vectorial properties [1].

Several salts have been prepared by acid-base reactions of triphenylguanidine with 1,2,4,5-benzenetetracarboxylic, cyanoacetic, diphenylacetic and trithiocyanuric acids, and their single-crystal X-ray structure analysis has been performed. Using the methodology that we have developed recently [2], we calculated the nonlinear susceptibility tensor components for the non-centrosymmetric salts. An Hirshfeld surface analysis [3] has been performed to study the effect of the various crystalline environments on the triphenylguanidinium cation, namely the effect of the hydrogen bonding motifs.

[1] Zyss J., *J. Chem. Phys.*, 1993, 98, 6583. [2] Pereira Silva P.S., Cardoso C., Silva M.R., Paixão J.A., Beja A.M., Garcia M.H., Lopes N., *J. Phys. Chem A*, 2010, 114, 2607. [3] McKinnon J.J., Spackman M.A., Mitchell A.S., *Acta. Cryst. B*, 2004, 60, 627.

Keywords: Hydrogen bonding, Nonlinear optical properties, Structure-physical properties relationships

FA4-MS33-P20

CRAFT database for development and testing force fields. Leonid Pereyaslavets, Alexei Finkelstein,

Institute of Protein Research RAS, Russia

E-mail: pereyaslavets.l@gmail.com

We collected a database of crystal structures and corresponding thermodynamic data at standard temperature for developing or testing various noncovalent force fields (FF). The FF must correctly predict the molecule-binding energy in crystals. The experimental energy of molecule binding in crystal is $\Delta U_{cryst-vap}^{exp} = -\Delta H_{sub} - (2 + n_{rot}/2) \cdot RT$, where n_{rot} is the number of free rotational degrees of freedom in the molecule, and ΔH_{sub} is the crystal sublimation energy per molecule. The latter expression is more precise than the conventional (see e.g., [1]) $\Delta U_{cryst-vap}^{exp} = -\Delta H_{sub} - 2 \cdot RT$. The FF-calculated energy of molecule binding in crystal is a difference between the minimized crystal energy per molecule and the minimized energy of the separate molecule in vacuum,

$\Delta U_{cryst-vap}^{calc} = U_{cryst} - U_{vap}$. The less is $|\Delta U_{cryst-vap}^{calc} - \Delta U_{cryst-vap}^{exp}|$ and geometric deviations from experimental crystal structure, the better the FF. Minimization of these deviations gives interaction parameters for the "in-vacuum" FF of any functional form. In the same way one can calculate thermodynamic potential, which describes the mean-force energy difference between molecule in crystal and in water, $\Delta U_{cryst-aq}^{exp} = \Delta U_{cryst-vap}^{exp} - \Delta G_{sol}$, where $\Delta G_{sol} = -RT \ln k_H$ is the free energy of solution of the molecule in water expressed via experimental Henry's law constant, k_H . The potential $\Delta U_{cryst-aq}^{exp}$ can be used for creating FF with implicit account of water environment [2]. We constructed a database that contains crystallographic structures and corresponding "in-vacuum" ($\Delta U_{cryst-vap}^{exp}$) and "in-water" ($\Delta U_{cryst-aq}^{exp}$) thermodynamic data extrapolated to a unified temperature (T=298K). Exploring of available thermodynamic and structural databases allowed us to collect the "in-vacuum" data for about a hundred and the "in-water" data for about sixty molecules. The resulting database CRAFT ("Crystals for Force Field Development and Testing") has been used for developing the empirical "in-water" force field FFSol [2] and testing the "in-vacuum" quantum-mechanical polarizable force field QMPFF3 [3]. This database is presented on the Internet page <http://www.craftdb.info>. It includes references to crystal structures (taken from the CSD database [4]), molecular properties (n_{rot} , etc.) and corresponding basic thermodynamic data (H_{sub} , k_H , etc.), as well as the resulting values $\Delta U_{cryst-vap}$, $\Delta U_{cryst-aq}$ at various conditions. Literature references are provided for all basic thermodynamic data, and the full path of calculation is provided for all calculated data. The major sources of data for sublimation enthalpy is the compilation of Chickos et al. [5] and for Henry's law constant the compilation of Sander [6].

[1] Ewig C.S. et al., *J. Phys. Chem. B*, 1999, 103, 6998. [2] Pereyaslavets L.B., Finkelstein A.V., *Molecular Biology*, 2010, 44, 303. [3] Donchev et al., *J. Comput. Chem.*, 2008, 29, 1242. [4] Allen, F.H., *Acta Cryst.*, 2002, B58, 380. [5] Chickos, J.S., Acree, W.E., Jr., *J. Phys. Chem. Ref. Data*, 2002, 31, 537. [6] Sander, R., 1999, <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>.

Keywords: force-fields, thermodynamic properties, Cambridge structural database

FA4-MS33-P21

Structural study of five novel spiro-1,2-**oxaphosphetanes.** Laura Rocés^a, Santiago García-Granda^a, Jesús García López^b, Antonio MoránRamallal^c, Javier González^c, Pablo M. Sansores Peraza^b,María José Iglesias^b, Fernando López Ortiz^b,^aDepartment of Physical and Analytical Chemistry,University of Oviedo, Spain; ^bÁrea de QuímicaOrgánica, Universidad de Almería, Spain; ^cDepartment

of Organic and Inorganic Chemistry, University of

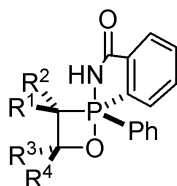
Oviedo, Spain

E-mail: roceslaura@uniovi.es

Carbonyl olefination of aldehydes and ketones by phosphorus ylides, the Wittig reaction [1], is a reference synthetic method for the regio- and stereodefined construction of carbon-carbon double bonds [2]. Despite being intensively studied for almost 60 years, the mechanism of this basic transformation in organic synthesis is still under debate. Most investigations

agree with a mechanism that involves a [2+2] cycloaddition to give a 1,2-oxaphosphetane intermediate. Those compounds are in general highly thermally labile species and only a small number of these intermediates have been isolated and structurally characterized through X-ray diffraction studies.

Here we report the full structural study of five novel spiro-1,2-oxaphosphetanes, including its electron density topological features [3]. The five oxaphosphetanes reported here present a distorted TBP structure with the oxygen and nitrogen atoms in the apical positions. The presence of the bidentate ligand ortho-benzamide contributes to stabilize the 1,2-oxaphosphetane ring.



- [1] Wittig, G. Geissler, G. *Liebigs Ann. Chem.* 1953, 580, 44. [2] Abell, A. D.; Edmonds, M. K. In *Organophosphorus Reagents*; Murphy, P. J., Ed.; Oxford University Press: Oxford, U.K., 2004; pp 99; Vedejs, E.; Peterson, M. J. *Adv. Carb. Chem.* 1996, 2, 1 [3] Menéndez-Velázquez, A.; García-Granda, S. *J. Appl. Cryst.*, 2003, 36, 193.

Keywords: oxaphosphetane, Wittig reaction, organophosphorus compounds

FA4-MS33-P22

Synthesis and Crystal Structure of aqua[N,N'-bis(3-methoxysalicylidene)-propane-1,2-diaminato]-methanholmanganese(III) perchlorate. Buket Safak,

Hulya Kara *Department of Physics, Balikesir University, Balikesir, Turkey*

E-mail: buketsafak@bau.edu.tr

The title compound, a hydrogen-bonded pseudo-dimer, $\text{Mn}(\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4)(\text{CH}_3\text{O})(\text{H}_2\text{O})\text{ClO}_4$ (I), has been structurally characterized. The compound I crystallizes in monoclinic space group $P2(1)/c$ with $a = 13.359$, $b = 13.338$, $c = 14.185$ Å, $\beta = 118.09^\circ$. In complex (I), the molecule comprises a manganese(III) centre coordinated by the nearly planar Schiff-base ligand [the angle between the least-squares planes of the aromatic rings of the ligands is 9.15°] with $\text{Mn}-\text{O}_{\text{phenol}}$ bond lengths of $1.870(4)$ Å and $1.869(4)$ Å, together with $\text{Mn}-\text{N}_{\text{imin}}$ bond lengths of $1.974(4)$ and $1.990(5)$ Å. The coordination sphere of the manganese centre is completed by a methanol molecule [$\text{Mn}-\text{O}_{\text{metoh}}$ $2.296(5)$ Å] and a water molecule [$\text{Mn}-\text{O}_{\text{water}}$ $2.208(3)$ Å]. The central Mn^{III} ion adopts an elongated octahedral coordination geometry, with the displacement of the Mn1 ion from the O1/N1/N2/O2 least-squares plane is $0.035(2)$ Å. In the crystal structure of (I), adjacent molecules are linked by hydrogen bonds [$\text{O}5\cdots\text{O}2^{\text{i}}$ = 2.969 Å, $\text{O}5\cdots\text{O}2^{\text{i}}$ = 2.916 Å, $\text{O}5\cdots\text{O}3^{\text{i}}$ = 2.898 Å and $\text{O}5\cdots\text{O}4^{\text{i}}$ = 2.883 Å; symmetry code, (i) $[-x+1, -y+1, -z]$], to form hydrogen-bonded pseudo-dimers, with additional face-to-face π - π stacking interactions between the benzene groups ($\text{C}6\cdots\text{C}10$ = 3.697 Å and $\text{C}5\cdots\text{C}11$ = 3.950 Å); symmetry code, (i) $[-x+1, -y+1, -z]$. Moreover, hydrogen bonds [$\text{O}6-\text{O}10\text{A}^{\text{ii}}$ = 2.871 Å] (ii) $[x+1, y, z]$ are formed between the axial methanol ligand and the perchlorate ion.

Keywords: crystal structure analysis, supramolecular chemistry, molecular magnets

FA4-MS33-P24

Structure and optical properties of natural low dimensional semiconductors. David G. Billing, Robert S. Black, *Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, PO Wits 2050, Johannesburg, South Africa*
E-mail: Dave.Billing@wits.ac.za

Inorganic-organic nanocomposite materials have been studied extensively in recent years because of the variety of interesting and useful properties associated with this family of compounds. The layered hybrids specifically the 2D $(\text{RNH}_3)_2\text{MX}_4$ and $(\text{NH}_3\text{RNH}_3)_2\text{MX}_4$ series, have shown good semiconduction, photoconductivity, photoluminescent and electroluminescent behaviour due to their inherent quantum well nature [1]. The quantum confinement of excitons in the 2D layers enhances the optoelectronic properties of the structure due to the enhanced binding energy. The nanocomposite method of synthesis is a bottom-up approach which produces multiple quantum well structures with predefined well thicknesses which is advantageous over the traditional MBE growth techniques which limits thickness. The manipulation of the barrier (insulator) layer is done by using various organic amine cations which enables adjustment of the well (interlayer) spacing and also has the ability to induce inorganic bond length, and bond angle distortions. Previously published results suggest [2-3] that the well (interlayer) $\text{X}\cdots\text{X}$ contacts play a large role in the shifting of the band gap at these short distances. A study of $(\text{X}-\text{C}_n\text{H}_{2n}\text{NH}_3)_2\text{PbX}_4$ (where $n = 2-6$ and $\text{X} = \text{halogen; OH}$) as a function of chain length and terminal halogen substitution gives insight into these interactions [4-5]. Optical experiments performed suggest the resultant photoluminescence emissions do not only change with the inorganic well (interlayer) spacing, but also has a strong conduction band mixing related to the (I^-X) interactions. These interactions give rise to intense sharp, but split emission lines, which are not necessarily just related to $\text{Pb}(6p) \rightarrow \text{Pb}(6s)$ emissions [69].

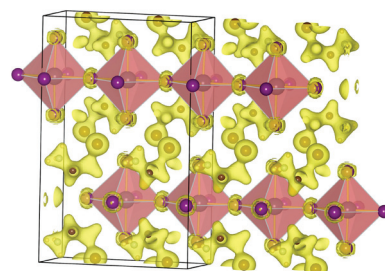


Fig. Charge density plot of $(\text{BrC}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4$

- [1] Mitzi D.B., *Progress in Inorganic Chemistry* 1999, 48, 1-121 [2] Xu Z, Mitzi D. B., and Medeiros D. R., *Inorg. Chem.*, 2003, 42, 1400-1402 [3] Louvain N, Mercier N, Boucher F, *Inorg. Chem.*, 2009, 48, 879-890 [4] Sourisseau S, Louvain N, Bi WH, et al., *Chem. Mater.*, 2007, 19, 600-607 [5] Sourisseau S, Louvain N, Bi WH, et al., *Inorg. Chem.*, 2007, 46, 6148-6154 [6] Ishihara T, Takahashi J, Goto T, *Solid State Communications.*, 1989, 69, 933-936 [7] Hong X, Ishihara T, Nurmikko A. V., *Phys. Rev. B.*, 1992, 45, 6961-6964 [8] Fujisawa J, Ishihara T, *Phys. Rev. B.*, 2004 70, 113203-113203, 4 [9] Fujisawa J, Tajima N, Tamaki K, Shimomura M, Ishihara T, *J. Phys. Chem. C.*, 2007, 111, 1146-1149

Keywords: Natural quantum wells, Inorganic-organic hybrids, Photoluminescence, Nanocomposites