

**m13.p32****X-ray diffraction and quantum chemical studies of interactions in polymorphs**G. Wójcik<sup>a</sup>, I. Mossakowska<sup>a</sup>, J. Szymczak<sup>a,b</sup>, S. Roszak<sup>a,b</sup>, J. Leszczynski<sup>b</sup><sup>a</sup> Institute of Physical & Theoretical Chemistry, Wrocław University of Technology, Poland. <sup>b</sup> Computational Center for Molecular Structure and Interactions, Jackson State University, Mississippi. E-mail: grazyna.m.wojcik@pwr.wroc.pl**Keywords:** polymorphism, interactions, TLS refinement

A crystal structure of an organic compound results from numerous, mainly weak interactions between molecules. The energy of interactions strongly depends on a distance between interacting molecules and atoms, so the contribution from the nearest neighbours is dominating. The statement is at the origin of our approach to the quantum chemical (MP2) calculations of the energy of interactions in the crystals under consideration. The experimentally determined crystal structures were assumed in the calculations. The two-body and three-body interactions were considered to represent the many-body interactions in the real crystal. We analysed molecular clusters, i.e. dimers and trimers formed by H-bonded and  $\pi$  stacked molecules in the polymorphs of *para*- and *meta*-nitrophenol [1,2]. The calculated energies of the intermolecular interactions within the clusters rationalise the polymorphic structures and may serve as a first-order approximation of crystal properties. The isostructurality of the stable forms of *para*- and *meta*-nitrophenol and, respectively, of their metastable forms is also reflected in the molecular translational and librational vibrations as well as in the internal, torsional vibrations of the nitro groups. The mean-square amplitudes of the vibrations were calculated from the variable-temperature anisotropic displacement parameters within the TLS formalism.

[1] Wójcik, G.; Holband, J.; Szymczak, J.; Roszak, S.; Leszczynski, J., *Cryst. Growth Des.*, 2006, 6, 274.[2] Wójcik, G.; Mossakowska, I. *Acta Cryst. B*, 2006, 62, 143.**m13.p33****Explaining the Packing of Tetrahedral Molecules**Alexandra Wolf<sup>1</sup>, Jürgen Glinnemann<sup>1</sup>, Martin U. Schmidt<sup>1</sup>, Jürgen Köhler<sup>2</sup><sup>1</sup> Institute of Inorganic and Analytical Chemistry, University of Frankfurt, Marie-Curie-Str. 11, D-60439 Frankfurt am Main. <sup>2</sup> MPI for Solid-State-Research, Heisenbergstr. 1, D-70569 Stuttgart. E-mail: wolf@chemie.uni-frankfurt.de**Keywords:** tetrahedral molecules, packing analysis, lattice energy calculations

In a preliminary search of the crystal structure databases CSD and ICSD, about 160 structures with neutral tetrahedral molecules of a single chemical species and with approximate point-group symmetry  $\bar{4}3m$  ( $T_d$ ) were found. Focus will be here on the crystal structures of  $EX_4$  molecules with  $E = C, Si, Ge, Sn, Pb, Ti$ , and  $X = H, F, Cl, Br, I$ , and on  $OsO_4$ .

The  $EX_4$  molecules exhibit in the solid state exact or rather near  $\bar{4}3m$  ( $T_d$ ) symmetry. Their crystal structures may be classified into five distinct types, if the arrangement of both, the  $E$  and  $X$ , atoms are considered. In many cases the molecules adopt a close packing; also the arrangement of the  $X$  atoms can be regarded as close packings. We found five distinct types for  $E/X$  arrangements: *hcp/hcp* ( $SnBr_4$ ), *ccp/ccp* ( $CF_4$ ), *ccp/bcc* ( $Cl_4$ ), *a<sub>1</sub>/ccp* ( $SnI_4$ ), *bcc/a<sub>2</sub>* ( $SiF_4$ ), including distorted variants. Besides the abbreviations *hcp* (hexagonal closed packing) etc., the symbols  $a_1$  and  $a_2$  denote more complex topologies unknown in the crystal structures of elements.

Lattice energy calculations with carefully adjusted force-field parameters were carried out in order to explain which packings are preferred for a given  $EX_4$  compound. We could also explain the polymorphism of  $GeBr_4$  [1, 2] and other molecules.

In the study of the crystal structures of molecules with increasing chemical complexity and more pronounced deviation from tetrahedral symmetry, quantitative indices for sphericity and tetrahedrality will be demonstrated to be useful.

Some results on lattice energy calculations on these compounds will be discussed.

[1] J. Köhler, H. Okudera, A. Simon: Crystal structure of germanium tetrabromide,  $\beta$ - $GeBr_4$ , low temperature modification, *Z. Kristallogr. NCS* 220 (2005), 524.[2] J. Köhler, H. Okudera, D. Reuter, A. Simon: Crystal structure of germanium tetrabromide,  $\alpha$ - $GeBr_4$ , room temperature modification, *Z. Kristallogr. NCS* 220 (2005), 523.