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Which Parameter to Select For Estimating the Degree of Strain in Substituted Tetrahydropyrans?

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A shift of atoms from position that mark their equilibrium coordinates increases the Gibbs free enthalpy of a structure. Such changes implied by intra- or intermolecular forces are evident from atomic parameter such as distances, bond or dihedral angles. For the six-membered cyclic ether tetrahydropyran, the chair conformation marks an undistorted molecular arrangement. Substituting a methyl group for a hydrogen atom, particularly in one of the axial positions, gives rise to changes in endo- and exocyclic dihedral angles, if referenced versus the undistorted chair geometry [1]. Since tetrahydropyrans, in particular those exhibiting multiple substitution at positions 2 and 6, constitute important natural products, we were interested to quantify strain induced by methyl substituents in tetrahydropyran. In the first part of the study, thermochemical and geometrical parameter were calculated for all isomers of dimethyltetrahydropyran using density functional theory [2]. The computed DG(298) values were correlated with bond and dihedral angles of the associated structures, in order to fit strain enthalpies to parameter that allow a classification of structures into *strained*, *medium-strained*, and *unstrained* isomers [2]. This information served as guideline for estimating the degree of strain of eight substituted tetrahydropyrans (X-ray analysis), in order find evidences for different efficiencies the compounds are formed in from alkenol bromocyclizations [3].

[1] Hartung, J., Greb, M., Svoboda, I., Fuess, H., *Acta Cryst.*, 2005, E61, o2770.

[2] Hartung, J., Bergsträßer, U., in preparation.

[3] Hartung, J., Greb, M., Svoboda, I., Fuess, H., in preparation.

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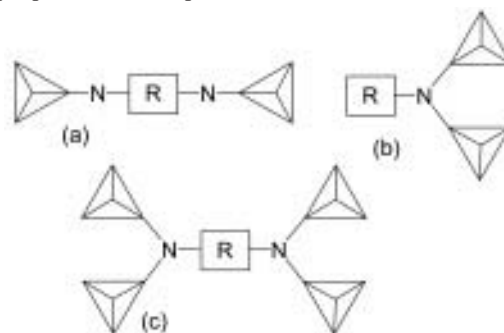
New inorganic-organic solids based on zirconium aminopolyphosphonates

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The use of amino or diamino polyphosphonate building blocks for the preparation of zirconium derivatives recently led to the disclosure of a vast class of insoluble inorganic-organic compounds featuring a wide structural variability [1-3]. Three different building block geometries were used in this study, as schematically reported in Figure. Diphosphonates (a) and (b) differ for the relative positions of the two phosphonate tetrahedra in the molecular fragment, while tetraphosphonate (c) is a combination of the first two geometries. The presence of only one organic R group for each two or four phosphonate tetrahedra induced the formation of low-dimensional inorganic-organic derivatives with a low density of organic moieties. In some cases, the formation of open framework structures was observed. Many of these structures were solved ab-initio from powder diffraction data. These compounds show a modular structure, in which composite inorganic building units are connected by organic groups in different ways, generating cavities and tunnels, whose dimension could be changed by varying the organic group. A survey of these new structures and their properties will be presented.



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[3] Vivani R., Costantino F., Costantino U., Nocchetti M., *Inorg. Chem.*, 2006, 45, 2388.