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Non crystallographic rotations observed between four *o*-halogen substituted tris-phenoxy-1,3,5-triazine derivatives

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A study of several disubstituted cycloalkanes led to a discovery of non crystallographic rotations [1]. Since the phenomenon was also observed in other systems (e.g. in isostructural rows [2]) it was termed *morphotropism* following Kitaigorodskii [3]. Later it turned out that Groth (1870) was the first to use the term *morphotropy* to describe the morphological changes of organic crystals, as the results of hydrogen substitution by e.g. Cl, Br, I in chemically allied compounds [4]. Without X-ray diffraction, the essence of morphotropy has remained pure speculation, however. The non crystallographic rotations, observed recently in a row of the *o*-halogen (F, Cl, Br and I) substituted tris-phenoxy-1,3,5-triazines, may shed light on Groth's conjecture. The F derivative crystallizes in triclinic unit cell ($P-1$, $Z=2$) which, on the F \rightarrow Cl replacement, is *doubled* in the *c*-axis. In the triclinic "Cl" lattice ($Z=4$) there are two symmetry independent pairs of molecules. They are related by a rotation of every second pair through *ca* 45° along the *ab* diagonal. The Cl \rightarrow Br replacement results in a second rotation of the same dimers through *ca* 90°, but perpendicular to the *ab* plane of a triclinic unit cell similar to "Cl" ($Z=4$), while the Br \rightarrow I change leaves the crystals *isostructural*. Thus, non crystallographic rotations which preserve similarity in *close packing* and result in an *isostructural* pair are the essence of *morphotropy* described gloomily by Groth and Kitaigorodskii. Grants No. OTKA T042642, T049712 and TÉT DAK-6/03 (OMFB-00527/2005).

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Dynamic charge density, a simple approach to chemical reaction mechanism

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The fast development of photo-induced and time resolved diffraction opens the fascinating questioning about the microscopic behaviour of systems out of equilibrium or undergoing a chemical reaction

The leading physical function is the time dependent charge density $\rho(r,t)$. We approach the problem through the simple reaction $H+H_2 \rightarrow H_2+H$. First we get an ab initio description along the reaction path, via the IRC defined by Fukui [1]. The knowledge of IRC allows for a control of the distance of approach of the projectile atom onto the target molecule, and thus for a connexion with reaction kinetics. We then model the geometry dependent charge density by a multicentre multipolar refinement (MOLLY). This leads to a simple description of multipole populations and effective radial shape as a function of geometry along reaction advance status.

The next phase consists in evaluation of the forces on various atoms as a function of IRC, through multipolar expanded charge density and Hellmann-Feynman approach. A simple qualitative model for geometry dependence of parameters is proposed, compatible with reaction kinetics, estimate of activation energy ... We are thus able to describe a reaction in terms of the unique function $\rho(r,IRC)$. The approach is then extended to more complex and realistic reactions, where the same unique function is the leading driving factor. It will progressively be affordable by scattering experiments and is moreover multi-disciplinary, since it allows for a correlation between X Ray scattering, quantum models and chemical reactivity. The approach is in phase with our recent contributions concerning the modelling of one particle density matrix from various experimental data [2].

[1] Fukui, A., *Accounts for Chemical Research* 1981, 14, 362.

[2] Gillet J.M., Becker P.J., *J.Phys. Chem. Solids*, 2004, 64, 2017.

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