

Looking for indirect correlations among charge density and NLO properties: the case of a simple pyridinium tetrazolate

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The development of novel second-order nonlinear optical (NLO) organic materials in the solid state is an important and growing research field, as it is attractive for laser industry, electro-optic devices, data safety issues, and so on. In recent decades, some experimental electron charge density studies have been performed on solid organic NLO-phores, aimed at extracting from the ground-state charge density the information on the hyperpolarizability tensor [Koritsanszky & Coppens, *Chem. Rev.* 101 (2001), 1583]. However, other groups [Whitten et al., *J. Chem. Phys.* 125 (2006), 174505, 1] claimed that the one-particle charge density does not contain sufficient information to determine the NLO properties. Even though it is impossible to obtain reliable quantitative approximations of the beta tensor elements directly from the charge density, it is also true that the former are influenced by the molecular structure and intermolecular interactions.

In this work, we look for possible indirect correlations between topological properties of the charge density and non-linear optical properties in a suitable, simple test-case. We focus on N-methyl pyridinium tetrazolate (PYRTE) [Beverina et al., *Chem. Comm.* 2011, 47, 292], a high optical gap chromophore exhibiting high thermal, chemical and photochemical stabilities, whose NLO are observable only in solution due to the centrosymmetric crystal structure. First, we investigate how the crystal field affects molecular dipole moment, and therefore optical properties, of the solid. As expected, the in-crystal molecular dipole moment undergoes a significant enhancement, determining an important change in the second-order tensorial parameters of PYRTE. We then compare the predicted hyperpolarizability of the title compound with that of suitable chemical derivatives. Possible correlations among non-local integral topological descriptors, such as the Source Function, and the computed second order hyperpolarizabilities are tentatively established. Eventually, we look for possible PYRTE derivatives that, while maintaining good predicted NLO properties, are also potentially able to crystallize in non-centrosymmetric space groups. To this end, the CLP model [Gavezzotti, *The Coulomb-London-Pauli (CLP) model of intermolecular interaction: Description and User's Manual v. 3.6.2013; Milano, 2013.*] is applied to rank *in silico* generated structures from a thermodynamic viewpoint.