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A charge density study of the effect of irradiation on the α-form of *p*-nitrophenol

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Abstract. Careful investigation of the structure and charge density of the α polymorph of *p*-nitrophenol has been carried out following prolonged irradiation by visible light. Though the change in colour from yellow to red is remarkable, the molecular geometry and the intermolecular hydrogen contacts exhibit only minor changes. However, a charge density analysis in comparison with the pristine α and β polymorphs has brought out significant differences in the charge distribution in the intra- and intermolecular bonding regions. The deformation density map of the α form reveals many differences in the bonding regions of the molecule before and after irradiation. Charge migration from the nitro and the hydroxyl groups to the phenyl ring of the molecule occurs on irradiation, resembling more the charge distribution in the light stable β form. The molecular dipole moment in the irradiated crystal is significantly lower compared to that before irradiation. Relief maps of the negative Laplacian in the hydrogen bond region also show less polarization of the oxygen lone pairs after irradiation.

Keywords. Crystal structure; charge density; *p*-nitrophenyl; polymorphism; photoirradiation.

1. Introduction

The experimental charge density method using X-ray diffraction to study chemical bonding in the solid state is becoming increasingly popular amongst chemists in recent years[1,2]. There have been a number of studies on a variety of materials of interest in quantum chemistry and medicine. Cameron and his coworkers[3], for instance, experimentally examined charge densities in aziridinyl, benzene and phosphazene rings and compared them with the theoretical values. Topological analysis of the charge distribution in maleate salts[4,5] has shown that short hydrogen bonds possess some covalent character. Charge density studies on L-dopa[6], vitamin C[7] and DL-aspartic acid[8] have been reported recently. Some workers have analysed non-centrosymmetric crystals of importance in nonlinear optics[9,10]. Recently, Coppens and coworkers[11] have carried out charge density studies on long-lived metastable excited states in nitrosyl complexes using synchrotron radiation.

We have been interested in investigating charge densities of organic crystals in relation to chemical reactivity and polymorphic forms. Recently, we reported a detailed investigation on the β and α polymorphs of *p*-nitrophenol using the charge density

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