

Role of urea molecule in co-crystals with dicarboxylic acids

Anna Krawczuk, Marlena Gryl, Katarzyna Stadnicka

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060, Krakow, Poland
e-mail: krawczuk@chemia.uj.edu.pl

Structural diversity of urea and dicarboxylic acid co-crystals has been a subject of many studies. Urea and dicarboxylic acids are considered as ideal candidates for forming co-crystals and are often used for crystal engineering purposes. Urea is a small, planar and bifunctional molecule where oxygen atom is a fourfold hydrogen bond (HB) acceptor, whereas nitrogen atoms are donors of four HBs. It has been shown¹ that the *syn* positioned HB donor and acceptor sites are employed in one dimensional chain formation, whereas anti-positioned HB donor and acceptor sites are responsible for the two and three dimensional crystal structures. Dicarboxylic acids on the other hand, possess two HB sites which are not used in the primary formation of an adduct, but assure the extension of this self-assembly in one and possibly two or three directions. Such a variety of behavior of urea and dicarboxylic acid in a crystal structure and combination of molar ratios, in many cases leads to multifunctional materials. For example co-crystal of urea and L-malic acid exhibits both linear and non-linear optical properties, the second harmonic efficiency at a fundamental wavelength of 1064nm is around three times that of KDP.² Similar nature reveal urea L-tartaric acid³ and urea DL-tartaric acid co-crystals⁴, for the second adduct SHG is one order of magnitude larger than that of KDP. Taking into account the fact that the urea molecule is a NLO chromophore⁵ we are especially interested in the change of electron density of urea in the solid state upon the choice of dicarboxylic acid and how those changes could influence physical properties of a given co-crystal.⁶

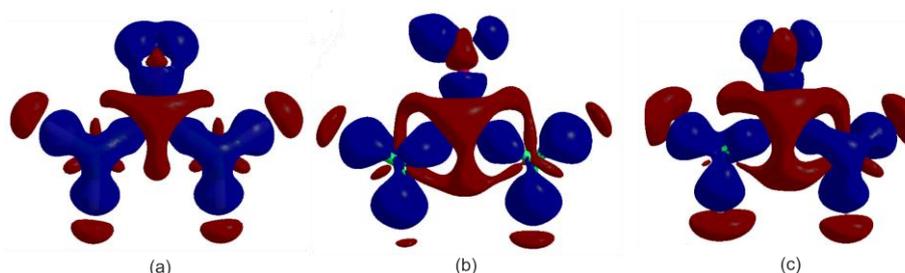


Figure 1 Static deformation electron densities of urea molecule for: (a) isolated molecule, (b) co-crystal of urea and oxalic acid and (c) co-crystal of urea and L-malic acid. Isosurfaces are drawn at $\pm 0.1 \text{ e}^- \text{ \AA}^3$. Red and blue colors indicate positive and negative regions.

¹Videnova-Adrabsinska V., Etter M. C. *J. Chem. Crystallogr.* 1995, **25**, 823-829

²Dixit V., Vanishri S., Bhat H., de Matos Gomes E., Belsley M., Santinha C., Arunmozhi G., Venkataramanan V., Proena F., Criado A. *J. Cryst. Growth* **2003**, *253*, 460–466.

³Lü M., Meng F., Zeng H., Yu W., *Chin Sci Bull*, 1996, **41**, 16, 1392-1395.

⁴Lü, M. K.; Mengz, F. Q.; Yangw, H.; Yu, T.; Zeng, H.; *Cryst. Res. Technol.*, 1996, **31**, 7, 833-836.

⁵Nie, W., *Adv. Mater* 1993, **5**, 520-545.

⁶Krawczuk A., Gryl M., Pitak M., Stadnicka K. *Cryst. Growth & Design*, 2015, submitted.