

s13.m36.o5 **The influence of ortho substituents on the twisting angle of a carboxyl group with respect to aromatic six-membered carbon rings.** Dirk J.A. De Ridder, Jesse Bos and Henk Schenk, *Laboratory for Crystallography, van 't Hoff Institute for Molecular Sciences, Faculty of Science, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands.* E-mail: dirkdr@science.uva.nl

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In 1995 we have shown that the out-of-plane rotation angle of a nitro group attached to aromatic six-membered carbon rings depends on the steric hindrance caused by one or two adjacent group(s), the electronegativity of the adjacent group(s) and the crystal packing [1]. In the present work we discuss the parameters influencing the rotation angle of a carboxyl group. Examples of aromatic six-membered carbon rings carrying a carboxyl group with (a) zero, (b) one and (c) two substituents in the ortho position have been retrieved from organic molecules in the Cambridge Structural Database [2]. General search restrictions ensured that for all entries the data were error-free, contained no metal(s), no polymers, crystallographic R value ≤ 0.075 , average estimated standard deviation for a C-C bond less than 0.005 Å, no additional ring fusion at aromatic ring carbon atoms. 266 Fragments of type (a), 299 fragments of type (b) and 38 fragments of type (c) have been used to examine the distributions of the rotation of the carboxyl group out of the aromatic plane, the carboxyl group bending out of the latter plane and the carboxyl group bending into this plane, resulting in different exocyclic angles. The analyses show that dipole-dipole interactions with the ortho substituent have a high influence whereas steric hindrance has a lesser importance. Moreover, benzoates (COO⁻) are rotated more out of the plane of the aromatic ring than acids (COOH).

- [1] D.J.A. De Ridder and Schenk, H. *Acta Crystallogr.* **1995**, B51, 221-231.
 [2] F.H. Allen and O. Kennard, *Chem. Des. Aut. News* **1993**, 8, 31-37.

s13.m37.o1 **Nanoscratching, a New Technique for Applied Crystallography.** Gerd Kaupp and M. Reza Naimi-Jamal, *University of Oldenburg, Fak. V, Org. Chem. I, D-26111 Oldenburg, P.O. Box 2503, Germany.* E-mail: kaupp@kaupp.chemie.uni-oldenburg.de

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Two dimensional transducers for nanoscratching experiments were first developed in 1997. Nanoindenters provide hardness and elasticity modulus that suffer from an "indentation size effect". We report now on diverse aspects of the new possibilities. Previously, the normal force was fitted to the indentation depth by a power series. However, a quantitative evaluation reveals now proportionality of normal force and (normal displacement)^{3/2}. The slope of the 1.5 exponential plot provides the indentation coefficient of dimension [$\mu\text{N}\cdot\text{nm}^{-1.5}$]. It represents the sensitivity of the crystal that differs on different faces. Interestingly, any kink in the 1.5 exponential plot points to pressure induced phase transformation, that can therefore be most easily detected. The 1.5 power law also scrutinizes the validity of the previously defined "friction coefficient (lateral force / normal force)" for all of the amorphous and varied crystalline materials (infinitely covalent, salts, metals, molecules with or without hydrogen bonding). It could be shown that the lateral force is proportional to the 1.5th power of the normal force upon constant-rate-nanoscratching. The slope of the 1.5 exponential plot with dimension [$\mu\text{N}^{-0.5}$] is the scratch coefficient. It quantitatively describes the crystal's response on different faces (e.g. of quartz) and in different directions depending on the anisotropy of the structure and is more precise than the "scratch resistance". Cleavage planes or channels are very important for the anisotropies in all types of crystals. The various features obtained on the same surface of molecular crystals depend primarily on the relative orientation of cleavage planes that may be normal, skew, or parallel under the surface. For example, on (110) of anthracene or thiohydantoin (exhibiting skew cleavage planes) one obtains either complete abrasion of material, or migration of molecules to both sides and in front, or only to the right, or only to the left side just by proper choice of the scratch direction. The migrated molecules coming up over the surface form solid hills on the surface that extend up to 5 or 10 μm from the scratched ditch and there is no loss of material. If the cleavage planes are vertical under the surface (an example is thiourea under (100)) molecular migrations to both sides or sharply in front occur when the scratching crosses or follows the cleavage plane direction. Exclusive abrasion (eventually with some loose deposit of debris) arises by scratching against skew cleavage planes or on layer surfaces and in the case of 3D-interlocked structures (without any possibility for migrations). Very detailed new effects of crystal dynamics are derived and can be used not only for diverse surface modeling in relation to the packing characteristics. Also the direct study of molecular migrations within crystals is an invaluable advance for the understanding of solid-state chemistry including face-selective chemistry both in salts and molecular crystals. The possibility for molecular migrations within the crystal is the basis for chemical solid-state reactivity, though. If migrations are structurally impeded no reactions can occur. The new experimental tool allows to study such migrations in more detail without the complications of molecular change.