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.