# Crystal Polymorphs of Metazachlor: Isolation, Morphology and Crystal Structure Analysis

**Ram K. R. Jetti [a], M. Haddow [b], P. Erk [b], V. Kahlenberg [c], K. Wurst [d], D. Weigand [a] U. J. Griesser [a]**

[a] Institute of Pharmacy, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria

[b] Research Center, BASF AG, D-67056 Ludwigshafen, Germany

[c] Department of Mineralogy, University of Innsbruck, Innrain 52, 6020 Innsbruck, Austria

[d] Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Austria

Metazachlor (MTZC, 2-chloro-N-(2,6-dimethylphenyl)-N-(1H-pyrazol-1-ylmethyl)-acetamide) is one of the most widely applied herbicides, selectively used against weeds in potato, rape, soybean and tobacco cultures.[1] The compound was found to exhibit five different polymorphs. Modification (mod.) I, II and III° can be crystallised from solvents and the melt, respectively, whereas the unstable mod. IV and V crystallise exclusively from the super cooled melt. Recently Griesser et. al[2] reported the thermodynamic stability of these polymorphs using different analytical techniques. This contribution deals with the follow up study of polymorphism in MTZC in terms of morphology, crystal structure, and powder X-ray diffraction measurements to reveal the structural features associated with modifications I, II and III°.

The high-temperature phase (Mod.I, m.p. 356 K, $\Delta_{fus}H$=19.7 kJ mol$^{-1}$) crystallises out of the melt when left at either room temperature (approx. 25 °C) or at refrigerator temperature (approx. 4-8 °C), in combination with other polymorphs. The pure mod. I can be obtained only by recrystallisation from solvents such as *n*-hexane and *n*-heptane, by slow evaporation of saturated solutions at room temperature. The thin flake like crystals obtained in this way turned out to be twinned by single crystal x-ray measurement and also sublimation produced similar poor quality crystals. Suitable crystals for a single crystal structure analysis were grown by slow evaporation of a saturated solution of *n*-heptane at 70 °C for three weeks, showing a plate like morphology. Mod. I crystallises in the orthorhombic space group *Pbca*. The experimental single crystal structure of mod. I exactly match with the structure calculated from the powder data using PowderSolve[3]. The crystal structure shows a columnar arrangement stabilised by weak C–H···O, C–H···N and C–H···$\pi$ interactions. Further, the Cl-group is involved in type-I,[4] Cl···Cl contacts merely contribute to close packing.

The lower melting modifications II and III° [II, m.p. 353 K, $\Delta_{fus}H$=23.0 kJ mol$^{-1}$; m.p. 349 K, $\Delta_{fus}H$=26.6 kJ mol$^{-1}$] were obtained by slow evaporation of a hot, saturated ethanol solution. Mod. II crystallises in triclinic space group $P\bar{1}$ with two molecules in asymmetric unit. The structure is stabilised by C–H···O, C–H···N and C–H···Cl interactions. Additionally the Cl-groups are involved in Cl···O interactions. Mod. III°, the thermodynamically stable form at room temperature, crystallises in monoclinic space group $P2_1/c$. C–H···O, C–H···N, C–H···Cl and C–H···$\pi$ interactions stabilise the structure in a head to tail fashion. The major difference between the three polymorphs is the mode of packing of the molecules in the crystal lattice which is due to significant conformational differences in the molecule (more likely around C–N bond). The experimental and calculated densities of the three polymorphs are in agreement with each other and follow the density-rule.[5] This rule should hold in particular for this molecule, since it contains no functional groups that are able to form strong interactions. Here, close packing, i.e. a maximum of weak interactions can be expected to determine the thermodynamic stability of the individual forms. All in all, MTZC, a flexible molecule with two degrees of acyclic torsional freedom would be a good candidate for conformational polymorphism.[6]

**References**


1. C. Tomlin (Ed.), The Pesticide Manual, 10th ed. British Crop Protection Council, Farnham, UK **1994**, p. 667.
2. U. J. Griesser, D. Weigand, J. M. Rollinger, M. Haddow and E. Gstrein; *J. Thermal. Anal. and Calor.,* **2004***, 77,* 511-512.
3. G. E. Engel, S. Wilke, O. König, K. D. M. Harris and F. J. J. Leusen*, J. Appl. Cryst*., **1999**, *32*,1169-1179.
4. R. Parthsarathi, G. R. Desiraju, *J. Am. Chem. Soc.,* **1989**, *111*, 8725-8726.
5. a) A. Burger and R. Ramberger, *Microchim. Acta, II,* **1979**, 259; b) A. Burger and R. Ramberger, *Microchim. Acta, II,* 1979, 273.
6. a) J. Bernstein, '*Conformational Polymorphism in Organic Solid State Chemistry*' (Ed.: G. R. Desiraju), Elsevier, Amsterdam, **1987**, pp. 471–518; b) J. Bernstein, *Polymorphism in Molecular Crystals*, Clarendon Press, Oxford, **2002**, pp. 151–187.