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# On the Polymorphism of Plant Protection Substances: Physicochemical Properties of Metazachlor Crystal Forms

D. K. Weigand, J. M. Rollinger and A. Burger

Institute of Pharmacy, University of Innsbruck, Josef-Moeller-Haus, Innrain 52, A-6020 Innsbruck, Austria

Metazachlor (2-Chlor-N-(2,6-dimethylphenyl)-N-(pyrazol-l-ylmethyl)acetamid) is a selective herbicide and widely used against weeds in the cultivation of potatoes, soya beans, maize or tobacco [1]. One of the preparative formulation of metazachlor is a flowable concentrate containing, 500 g active ingredient in the crystalline state per liter formulation (Butisan S®).

Metazachlor was found to exist in five modifications, which were investigated and characterized by thermomicroscopy, DSC, vibrational spectroscopy, X-ray diffractometry and pycnometry. Mod. I, II and III crystallize from solvents whereas the unstable mod. IV and V crystallize from the super-cooled melt. Based on the results of thermal analysis and solvent mediated transformation studies, the thermodynamic relationships among the polymorphic phases of Metazachlor were evaluated and verified in a semi-schematic energy/temperature-diagram [2J.

At room temperature, mod. Ill (m.p. 76°C, $\Delta_{fus}H_{III}$= 26.6 ± 0.2 kJ $mol^{-1}$) is the thermodynamically stable crystal form, followed by mod. II (m.p. 80°C, $\Delta_{fus}H_{II}$ 23.0 ± 0.3 kJ $mol^{-1}$) and mod. I (m.p. 83°C, $\Delta_{fus}H_{I}$ = 19.7 ± 0.1 kJ $mol^{-1}$). According to the heat-of-fusion rule [3], these three modifications are enantiotropically related, respectively. This agrees with the order of densities (density rule, [3]) and is also confirmed by the endothermic transition from mod. Ill into I (7.4 kJ $mol^{-1}$, heat-of-transition rule, [3]). By stirring aqueous suspensions of mod. I, II, III, and their mixtures, the following thermodynamic transition point intervals were determined: $T_{trs,\ III-II}$ 57 to 61°C, $T_{trs,\ III-I}$ 60 to 65°C and $T_{trs,\ II-I}$ 61 to 67°C. These values are in accordance with the transition points calculated from the melting points and heats of fusion [4]. It is likely that mod. IV (m.p. 74°C, $\Delta_{fus}H_{VI}$ -18.7 ±0.7 kJ $mol^{-1}$) and mod. V (m.p. 65°C) are monotropically related to each other as well as to mod. I, II and III.

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