

# CONFORMATIONAL COLOR POLYMORPHISM AND SOLVATES OF PICRYLTOLUIDINE

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P-tolyl-(2,4,6-trinitro-phenyl)-amine (Picryltoluidine, PT), is an intriguing example of conformational polymorphism exhibiting two differently colored crystalline modifications, a red ( $I_R$ ) and an orange ( $II_O$ ). So far only the cell dimensions of two polymorphs have been reported in the literature, and in the Cambridge structural database only the  $I_R$  can be found, yet without atomic coordinates [1, 2]. The reinvestigation of this compound resulted in five new unstable solvates in addition to the two known polymorphic modifications. It was possible to obtain single crystal structures of all seven forms, which were also characterized by a variety of other analytical techniques such as thermal analysis (hot stage microscopy, DSC, TGA), vibrational spectroscopy (IR, Raman) and X-ray powder diffractometry.

PT mod.  $I_R$  (space group  $P2_1/a$ ) and mod.  $II_O$  ( $P2_1/c$ ) show each one conformer in the asymmetric unit. The solvates (formed with pyridine, benzene, toluene, xylene and chlorobenzene) are isostructural ( $C2$ ), except the pyridine solvate ( $P2_1/a$ ). The solvent molecules are either located in channels (isostructural solvates) or in layers (pyridine solvate) from where they can escape easily. Additionally, intra-molecular hydrogen bonds of the type  $N-H\cdots O$  and short intermolecular interactions  $C-H\cdots O$  and  $\pi\cdots\pi$  stacking stabilize all crystal structures. The picryltoluidine/solvent ratio was confirmed with TGA experiments. The four isostructural solvates show a ratio of 2:1, whereas the pyridine solvate shows a 1:1 ratio. The pyridine solvate desolvates to the higher melting mod.  $I_R$  ( $T_{fus}$ : 165.5°C,  $\Delta_{fus}H$ : 31.3 ± 0.1 kJ·mol<sup>-1</sup>), whereas the four isostructural solvates desolvate to the metastable mod.  $II_O$  ( $T_{fus}$ : 163.5°C,  $\Delta_{fus}H$ : 28.6 ± 0.1 kJ·mol<sup>-1</sup>). From the heat of fusion rule [3, 4] it is obvious that the two forms are monotropically related. However, the calculated densities of the two polymorphs do not follow the density rule, this could possibly be due to the overall hydrogen-bond contribution which is higher in form  $II_O$ . Due to the presence of strong intramolecular  $N-H\cdots O$  hydrogen bonds, the IR-spectra of the polymorphs show clear differences. A short  $N-H\cdots O$  hydrogen bond in mod.  $II_O$  ( $\nu_{N-H}$ : 3257 cm<sup>-1</sup>) results in a hypsochromic (blueshift) shift of the  $\nu_{N-H}$  band of 66 cm<sup>-1</sup> with respect to mod.  $I_R$  (3323 cm<sup>-1</sup>). This correlates with the color change in these modifications due to differences in the charge transfer interactions.

## References

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