

STRUCTURAL CHARACTERIZATION OF A MONOCLINIC POLYMORPH OF CITRACONIC ACID

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As part of our work on the synthesis of metal derivatives of unsaturated dicarboxylic acids, at room temperature and under solvothermal conditions, we routinely carry out the characterization of reagents and reaction products by spectroscopic, thermal, and X-ray diffraction techniques. We noticed that the X-ray powder pattern of commercially obtained citraconic acid (**1**), was similar to the unindexed pattern reported by Rose in the ICDD Powder Diffraction File (PDF-4, 00-037-1909). However, it was different from the calculated pattern obtained using the data reported by Batchelor and Jones (1) (REFCODE: NEDNOZ) downloaded from the Cambridge Structural Database (This is the only report found in the Cambridge Structural Database (CSD) for citraconic acid). This finding indicated that the commercial material is a different polymorph of citraconic acid. Attempts to grow single crystals of this form in several solvents (water, methanol, ethanol and ethyl acetate) led invariably to the triclinic phase reported by Batchelor and Jones.

The pattern of the reagent provided by the commercial vendor was indexed with DICVOL 06, and it showed that the material crystallizes in the monoclinic system, with unit cell parameters $a=8.304$, $b=7.104$, $c=10.841$ Å, $\beta=114.31^\circ$. The cell volume is more than twice the cell volume of the material obtained by Batchelor and Jones. The final figures of merit obtained after the analysis carried out with the program NBS*AIDS83 were $M_{20} = 22.3$; $F_{30} = 36.1$ (0.0170, 49). Single crystal synchrotron data was collected on a small fragment at the Advanced Photon Source of Argonne National Laboratory as part of the SCrAPS program. The two polymorphs differ in the hydrogen bonding scheme. While in the triclinic polymorph both carboxylic groups participate in cyclic hydrogen bonds, in the monoclinic polymorph there are two types of intermolecular hydrogen bonds. The structural features will be discussed in detail.

(1) Batchelor, E.; Jones, W. (1998) *Acta Cryst.* **C54**, 238-240.

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