

Determination of the Absolute Crystal Structure of Achiral Pentaerythritol

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This investigation was carried out in a larger framework aiming for the correlation of the optical rotation of the achiral molecule Pentaerythritol (PE, $C(CH_2OH)_4$) to the crystal and molecular structure. PE is a compound with a tetrahedral coordination of the central carbon atom by four hydroxymethylene groups which are chemically equivalent and related to one another by the second kind symmetry operation $\bar{4}$. While the optical rotation of an achiral molecule or ensemble of molecules may sound strange to some, it was predicted by Gibbs for point groups $\bar{4}$ and $\bar{4}2m$ [1] and demonstrated not until 85 years later [2].

The effect of the optical rotation of PE which crystallizes in space group $I\bar{4}$ has been determined in the Department of Chemistry, University of Washington, Seattle from a ca. 5 mm large crystal plate of 0.5–0.7 mm thickness. In order to measure the tiny optical rotation of the pure C-O-H-compound PE a special method called high-accuracy universal polarimetry (HAUP) had to be applied [3].

PE is the simplest organic crystal, with only three independent non-hydrogen atoms, for which the complete optical rotation tensor has been determined, and it is the only achiral molecular crystal so analyzed. PE molecules have the full site symmetry of the crystallographic point group and thus the crystal tensor may be analyzed as a simple sum of its molecular contributions. Since the molecule is comparatively simple in its molecular and electronic structure the chiroptical properties are also accessible by quantum mechanical analysis e.g. [4].

For these analyses the optical rotation measured relatively to the macroscopic crystal faces has to be correlated to the orientation of the molecule in the crystal absolutely. For this investigation the marked pieces of the crystal used for the optical measurements were available to carry out a crystallographic intensity data collection at beamline PETRA 1, which is summarized in Table 1. A projection of the molecule is shown in Fig. 1. The lattice of the Pentaerythritol crystals shows the full tetragonal symmetry (holohedry $4/m\ 2/m\ 2/m$). Since the symmetry of the crystal structure is only $\bar{4}$ there exists a manifold ambiguity in selecting the coordinate system. Space group $4/m\ 2/m\ 2/m$ can be decomposed in 4 cosets relative to space group $\bar{4}$. Each symmetry element of the cosets not equal to $\bar{4}$ itself are possible ambiguities for an absolute assignment of the coordinate system relative to the molecule. The ambiguity due to the coset that can be generated

space group	$I\bar{4}$	temperature	RT
a, b	6.084(1) Å	c	8.747(1) Å
wavelength	0.5888 Å	detector	165 mm MarCCD
diffractometer	6-circle	max. resolution	0.55 Å
no. of measured reflections	5654	no. of unique reflections	950
completeness	97%	R_{int}	1.4%
mean $I/\sigma(I)$	60	no. of parameters	34
R-value	3.1%		

Table 1: Summary of the data collection and refinement statistics of Pentaerythritol.

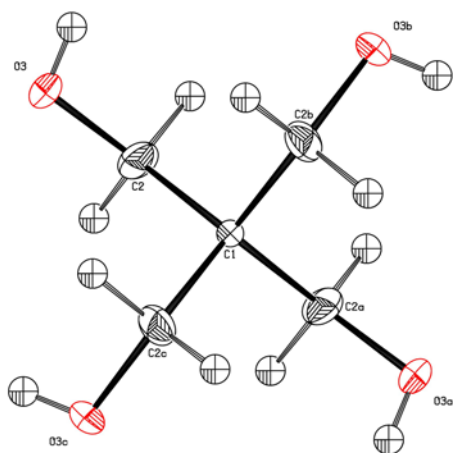


Fig. 1: Projection of the Pentaerythritol molecule with 50% probability displacement ellipsoids for non-H atoms [5].

e.g. by the two fold axis in x-direction can be resolved by comparing measured and calculated reflection intensities even if the difference is only due to the single H-atom bound to O3 (see Fig. 1). The remaining ambiguities only manifest themselves in intensity differences of Friedel opposites which are very small in case of a light atom structure like PE. Another method to resolve this problem is the direct measurement of triplet phases by three beam diffraction experiments [6, 7]. As this method measures directly invariant triplet phases it is independent of any anomalous dispersion effects. However, the crystals or parts of them have to be of very low mosaicity. The above mentioned ambiguity gives rise to a different sign of the triplet phase. In Fig. 2 typical three-beam interference profiles of PE measured with the 6-circle diffractometer at beamline PETRA1 is shown. The constructive and destructive interference patterns allow an unambiguous assignment of the molecules orientation relative to the axis and the macroscopic crystal faces, respectively. Further details of this experiments and more information on the evaluation of the optical rotation of PE have been published in [8].

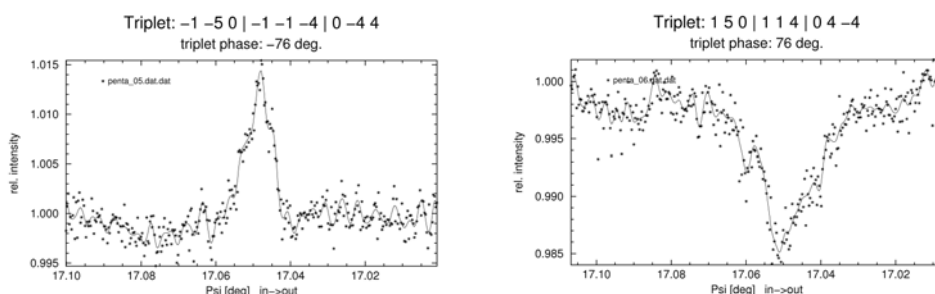


Fig. 2: Example of a centrosymmetrically related pair of three-beam interference profiles for PE.

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