

06.6-03 ACCURATE DETERMINATION OF HYDROGEN POSITIONS FROM X-RAY DATA. II. PENTAERYTHRITOL. By Håkon Hope and Brenda G. Nichols, Department of Chemistry, University of California at Davis, Davis, CA 95616, USA.

In a previous report from this laboratory the successful determination of positions of H bonded to C or N using a spherical atom model was reported (Hope and Ottersen, Acta Cryst. (1978) B34, 3623). Attempts to position H in OH groups had been unsuccessful. For further study of this problem we have chosen pentaerythritol, $C(CH_2OH)_4$. The compound has only $\frac{1}{2}$ molecule per asymmetric unit, and was expected to be crystallographically well behaved (Eilerman and Rudman, Acta Cryst. (1979) B35, 2458).

All unique reflections accessible with MoK α to $2\theta = 163^\circ$ (~ 1700) were measured on a Picker diffractometer (graphite monochromator, temp. 85 K, θ - 2θ scan $2^\circ/\text{min}$ in 2θ , spherical crystal $r \sim 0.28$ mm). Only 3% of the intensities had $I < \sigma(I)$, 85% had $I > 6\sigma(I)$. The intensities were corrected for scan truncation errors (Denne, Acta Cryst. (1977) A33, 438).

Full-matrix least-squares refinements were performed with anisotropic temperature factors for C, O, and isotropic for H. In keeping with previous experience the H(C) atoms could be well determined by excluding data below $S = \sin \theta/\lambda = 0.65 \text{ \AA}^{-1}$, while the O-H distance was too short ($\sim 0.90 \text{ \AA}$). Calculations with varying S_{min} showed the largest deviations to occur for $S_{\text{min}} 0.55$ - 0.60 \AA^{-1} , and that acceptable results were obtained with $S_{\text{min}} = 0.75 \text{ \AA}^{-1}$ (O-H = $0.98(3) \text{ \AA}$).

Hope and Ottersen (ibid) had assumed that a very high observations/parameters ratio is needed for this type refinement. We tested this assumption by also imposing a maximum value on S. For a wide range of S_{max} there was little effect on the H positional parameters; e.g. the results from the data in the 0.7 - 0.8 \AA^{-1} shell (129 reflections, 33 parameters) were essentially the same as those obtained with all data above 0.7 \AA^{-1} . This probably stems from the fact that the thermally damped scattering factor for H falls off rather rapidly at higher S values, so that virtually no added information is contained in data above, say, 1 \AA^{-1} . The magnitude of the H temperature factor is a critical parameter here. The small number of observations per parameter required presumably reflects the low counting statistics errors of our data.

In order to determine the cause for the dependence of H(O) parameters on S_{min} we computed difference electron density maps with C, O (high order parameters) subtracted, varying S_{min} from 0.5 to 0.8 \AA^{-1} for reflections included. In the O-H region two peaks appeared, one near the presumed H nuclear position, and one halfway between O and H. The bond peak persisted to about $S_{\text{min}} = 0.7 \text{ \AA}^{-1}$, and with $S_{\text{min}} = 0.6 \text{ \AA}^{-1}$ the two peaks were of nearly equal height. Toward higher S_{min} values the bond peak diminished much more rapidly than the 'nuclear' peak. Apparently the refinement program places the H atom near the center of gravity of the two peaks, with undesirable consequences if an inappropriate S_{min} is chosen.

The approach described here (spherical atom model, very good data in the 0.7 - 0.9 \AA^{-1} range) is expected to yield reliable results unless high H thermal motion precludes significant H contribution to the structure factors.

More realistic models for the atomic form factors may lessen the requirements for good counting statistics (e.g. Hirshfeld and Hope, Acta Cryst. (1980) B36, 406).

06.6-04 CORRECTIONS FOR THERMAL DIFFUSE SCATTERING IN THE LWD APPROXIMATION. By R.B. Helmholtz, Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands, and A.W.M. Braam and Aafje Vos, Laboratorium voor Chemische Fysica, Nijenborgh 16, 9747 AG Groningen, The Netherlands.

It has been shown by Kroon and Vos (Acta Cryst. (1979), A35, 675-684) that corrections for first order thermal diffuse scattering (TDS) for X-ray diffraction intensities of molecular crystals can be calculated in very good approximation by the LWD model. In this model the acoustic branches are considered only; long wave behaviour is assumed for the eigenvectors, but the actual dispersion is taken into account for the frequencies. For linear frequency dispersion with $v_j(\underline{g}) = v_j(\underline{\hat{g}})g$ and neglect of quantum effects the contribution to $\alpha_1(\underline{H})$ of the pyramids around \underline{g} and $-\underline{g}$, each having a solid angle $d\Omega(\underline{g})$, is given by

$$\alpha_1(\underline{H}, \underline{g}) d\Omega(\underline{g}) = \frac{2k_{\text{TH}}^2 G}{\rho} \sum_{j=1}^3 \frac{|\hat{u}_j(\underline{\hat{g}}) \cdot \underline{\hat{p}}|^2}{v_j^2(\underline{\hat{g}})} d\Omega(\underline{g}). \quad (1)$$

For derivation and symbols used see Helmholtz and Vos (Acta Cryst. (1977), A33, 38-45). Account of the actual frequency distribution $v_j(\underline{g})$ changes $1/v_j^2(\underline{\hat{g}})$ in (1) to

$$I_j(\underline{\hat{g}}, G) = G^{-1} \int_0^G (g^2/v_j^2(\underline{g})) dg \quad (2)$$

where G is the maximum value of \underline{g} . The frequency distribution has to be measured by inelastic neutron scattering, which is not easy to accomplish for molecular crystals. It can also be found by lattice dynamical calculations. The program LATDYN developed by Kroon (see Kroon and Vos) has been extended in such a way that molecules with charged atoms can be treated. To this end the convergence acceleration technique described by Williams (Acta Cryst. (1971), A27, 452-455) has been added to the minimization procedure, and in the calculation of the dynamical matrix complete rigid body molecules are taken into account instead of all atoms within a certain distance from the atom considered. For different directions $\underline{\hat{g}}$ in reciprocal space $I_j(\underline{\hat{g}}, G)$ is calculated as a series expansion in G. The summation technique of the program TDS2 developed by Helmholtz (see Helmholtz and Vos) is used for the computation of $\alpha_1(\underline{H})$. Results for naphthalene for different atom-atom interaction functions and different samplings of the directions $\underline{\hat{g}}$ for the numerical integration will be presented.