

06.6-01 AN ELECTRON DENSITY STUDY OF α -OXALIC ACID DIHYDRATE. By J. Dam, S. Harkema and D. Feil, Chemical Physics Laboratory, Twente University of Technology, Enschede, The Netherlands.

In this X-ray electron density study of α -oxalic acid dihydrate, which is a contribution to the Oxalic Acid Project of the Commission on Charge, Spin and Momentum Densities, extensive intensity measurements were done on a PW1100 4-circle diffractometer. [Mo K_{α} radiation; $\theta/2\theta$ step-scan technique; graphite monochromator]. Each reflection in the whole reciprocal sphere up till $\sin \theta/\lambda = 1.3 \text{ \AA}^{-1}$ was measured for (at most) 5 different orientations of the crystal (by turning about the scattering vector) amounting to a total of 46994 intensities. Corrections were made for a decrease in intensity of about 4% as revealed by repeatedly measured standard reflections. Furthermore absorption and beam-inhomogeneity corrections (I) were performed. Averaging symmetry related intensities yielded 3304 independent reflections with internal agreement factor $R(I) = 3.1\%$.

Positional parameters, as derived from high order refinements ($\sin \theta/\lambda > 1.0 \text{ \AA}^{-1}$) agree with the X-ray results of Stevens & Coppens (2) within 0.0007 \AA , while comparison with neutron results of Feld (3) and of Koetzle & McMullen (4) shows maximum difference in positional parameters of 0.002 \AA and 0.0015 \AA respectively.

Comparing thermal parameters we find for the ratio $U_{ii}(\text{our results})/U_{ii}(\text{others})$, averaged over the non-hydrogen atoms:

		U_{11} -ratio	U_{22} -ratio	U_{33} -ratio
Stevens & Coppens (2)	(X-ray)	0.927(6)	0.921(7)	0.982(7)
Feld (3)	(Neutron)	1.050(8)	1.123(8)	1.077(4)
Koetzle & McMullen (4)	(Neutron)	0.951(7)	1.027(3)	1.037(3)

As an illustration of good agreement with respect to electron density features an experimental deformation map in the plane of the oxalic acid molecule is shown in Fig. 1, which can be compared with Fig. 1 of Stevens & Coppens.

Further experimental detail, as well as the results of a Hirshfeld-type deformation analysis and of SCF-X α -LCAO quantum chemical calculations will be presented.

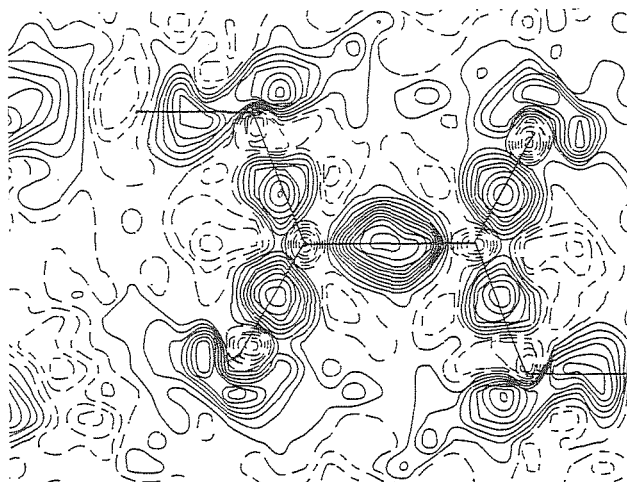


Figure 1

- (1) S. Harkema, J. Dam, G.J. van Hummel and A.J. Reuvers, Acta Cryst. A36 (1980) 433.
- (2) E.D. Stevens and P. Coppens, Acta Cryst. B36 (1980) 1864.
- (3) R.H. Feld, Ph.D. Thesis, University of Marburg (1980).
- (4) T.F. Koetzle and R.K. McMullen, Oxalic Acid Project Circular (1980).

06.6-02 ON DATA REDUCTION AND ERROR ANALYSIS FOR SINGLE CRYSTAL DIFFRACTION INTENSITIES. By Robert H. Blessing and George T. DeTitta, Medical Foundation of Buffalo, Inc., 73 High St., Buffalo, NY 14203, USA.

Crystallographic studies aimed at detailed mapping of the electron density in molecules and crystals require unusually careful efforts to eliminate systematic experimental errors and to recognize and minimize random errors. Several methods for estimating Bragg peak limits in step-scanned reflection profiles have been developed: minimization of $\sigma(I)/I$ [Lehmann & Larsen (1974) Acta Cryst. A30, 580]; location of the changes from decreasing peak intensity to "probably constant" background intensity [Grant & Gabe (1978) J. Appl. Cryst. 11, 114]; and minimization of an autoconvolution of the intensity profile [Rigault (1979) J. Appl. Cryst. 12, 116]. These methods become less reliable as peak-to-background values diminish, but, given limits for a suitable sample of the prominent peaks in a data set, anisotropic reflection width parameters can be found by least-squares fit and used to calculate peak limits for even the weakest reflections. To observed base widths W_1 and W_2 below and above the centroids of the "good" peaks, we fit coefficients q_{ijk} and T_i according to

$$W_i = Q_i + T_i \tan \theta \quad i = 1, 2$$

$$Q_i = \sum_{j=1}^3 \sum_{k=1}^3 Z_j Z_k q_{ijk} = Z^T Q Z$$

The quantities Z_j are components along crystal-fixed Cartesian axes of a unit vector normal to the incident and diffracted beams. For diffractometer axes defined as in the International Tables for X-Ray Crystallography [Vol. IV, pp. 276-278 (1974)], the Z_j are given by

$$(Z_1, Z_2, Z_3) = (\sin \phi \sin \chi, \cos \phi \sin \chi, \cos \chi).$$

Our estimates of $\sigma^2(I)$ include contributions from: (1) the Poisson variance of the stepwise count rates, corrected for coincidence losses; (2) the variance of the measured dead time of the counting chain, and the variance of the correction factor for the beam attenuator, if used; (3) the variances and covariance of the parameters of a straight line fitted to the background; (4) the variances and covariances of the parameters of polynomial scaling functions of X-ray exposure time fitted to the periodically measured reference intensities; (5) the mean square deviation from the mean of the scaling factors derived from these functions; and (6) the instrumental variance $p^2 I^2$ [McCandlish, Stout & Andrews (1975) Acta Cryst. A31, 245]. Research supported by NIH Grant No. AM-19856.