Note on the Oxygen Lone-Pair Densities Observed in
trans-2,5-Dimethyl-3-hexene-2,5-diol Hemihydrate, $C_8H_{16}O_2 \cdot \frac{1}{2}H_2O$

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Abstract

Improved experimental dynamic deformation density maps of the title compound are compared with theoretical static density maps computed for a molecular cluster with an extended basis set. No conclusive evidence has been obtained on a possible polarization of the oxygen lone-pair electrons towards the hydrogen bonds.

Introduction

Some years ago, van der Wal & Vos (1979*a*, *b*; hereafter referred to as WV*a* and WV*b* respectively) reported the deformation density in crystals of the title compound (II-*trans-A* .½H₂O) at 86 K. The structure is given in Fig. 1. In the present study, improvements have been made in the profile analysis of overlapping reflections by considering the minimum of the smoothed intensity profile between these reflections as the best estimate of the background at this position. In the earlier study, this background was taken from a region around the minimum (for details, see van der Wal, 1982). The deformation density map for the central part of the molecule does not show essential changes. In contradistinction to WV*b*, in which hydrogen bonds around the water molecule were not investigated, all hydrogen bonds are considered in the present paper.
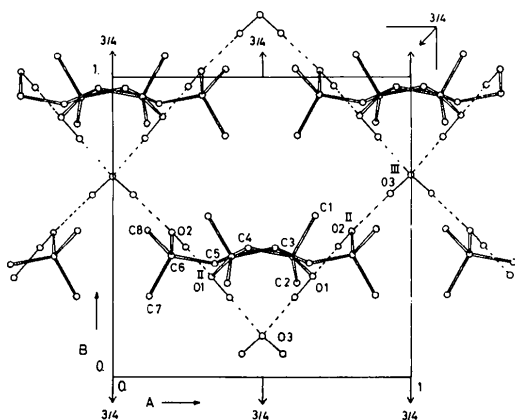

Fig. 1. Projection of the layer around $z = \frac{1}{4}$ in the structure of II-*trans-A*.½H₂O, along [001] onto the plane (001); $O^{II} = O(\bar{x} + 1, y, z + 1\frac{1}{2})$, $O^{III} = O(x + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + 1\frac{1}{2})$. Reproduced from WV*a*, Fig. 1. See WV*a* for the geometry of the hydrogen bonds.

Experimental and theoretical density maps

The experimental filtered deformation density distribution is calculated by use of the formula:

$$D_{fl}(\mathbf{r}) = \frac{1}{V} \sum_H [F_c(\text{rel; total model})/k$$
$$-F_c(\text{abs;IAM};\mathbf{r}_{HO}; U_{HO})]$$
$$\times \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}). \quad (1)$$

The F_c(rel;total model) values are based on the parameters of a full-angle multipole refinement with the program *VALRAY* (Stewart, 1976) in which in addition to the deformation parameters the atomic coordinates and the thermal parameters were varied.* Model calculations on Si–O (van der Wal, 1982) have shown that filtered deformation density maps obtained in this way reveal all systematic features present in the experimental data, even for deficient multipole models. The F_c(abs;IAM;$\mathbf{r}_{HO}$;U_{HO}) values are based on the independent atom parameters obtained from conventional high-order refinements ($\sin \theta/\lambda = 0.7$–$1.08$ Å⁻¹). Sections through the O lone-pair regions and the O $\cdots$ H–O bonds are shown in Fig. 2. The figure shows a slight tendency for the O lone-pair electrons to be polarized towards the hydrogen bonds. It is not certain, however, whether these polarizations are significant. Calculation of filtered maps around O(3) for different y[O(3)] showed changes of approximately 0.05 e Å⁻³ in the lone-pair maxima for $\Delta y = 0.001$ Å, which shift is about equal to the standard deviation of 0.0007–0.0008 Å found for the oxygen HO coordinates. Moreover, the dipolar and quadrupolar deformations around O are likely to be reduced because of correlation between these deformations and the HO positional and thermal parameters for O [compare, for instance, the *X–N* and *X–X* maps of cyanuric acid (Coppens & Vos, 1971)].

The static theoretical deformation density map is defined as

$$D_{th}(\mathbf{r}) = \rho_{th}(\text{cluster};\mathbf{r}) - \rho_{th}(\text{atoms};\mathbf{r}). \quad (2)$$

* Lists of structure factors, a table with details of the refinements, a table with non-H IAM parameters with bond lengths and angles, and additional sections of $D_{fl}(\mathbf{r})$, $D_{th}(\text{Hb};\mathbf{r})$ and $D_{th}(\mathbf{r})$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38629 (55 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
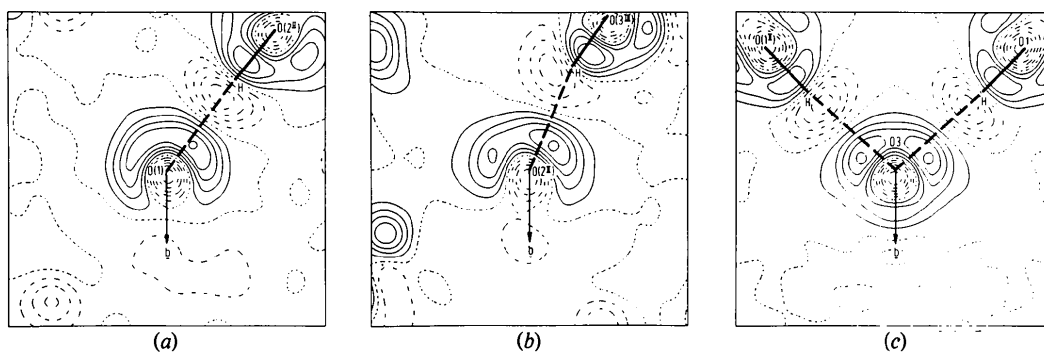
Fig. 2. Sections of the $D_n(r)$ map through the lone-pair regions of O. Contours at intervals of 0·05 e Å⁻³. Full lines give positive, and dashed lines negative values. The zero line is dotted. (a) Plane through the bisector **b** of C(3)O(1)H and O(1) · · · H; O(2^{II}) at distance of −0·024 Å from plane. (b) Through **b** of C(6^{II})O(2^{II})H and O(2^{II})· · ·H; O(3^{III}) at −0·167 Å from plane. (c) Through **b** of HO(3)H and O(3)· · ·H; O(1) at 0·073 Å from plane.
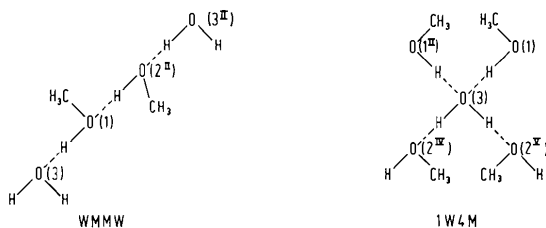

Fig. 3. Clusters WMMW and 1W4M used in the theoretical calculations. Compare with Fig. 1. O(2^{IV}) is related to O(2) by the b glide plane at $x = \frac{1}{4}$; whereas O(2^V) is related to O(2^{IV}) by the twofold axis through the water molecule.

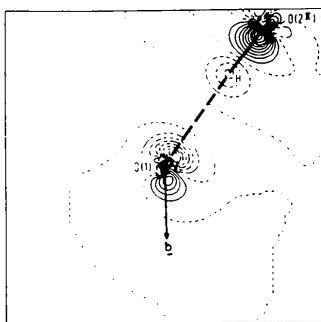Fig. 4. Section of the $D_{th}(Hb;r)$ map through **b** of C(3)O(1)H of cluster WMMW and O(1)· · ·H. Contours at intervals of 0·05 e Å⁻³. In $D_{th}(Hb;r)$ around O(3) of cluster 1W4M similar features, but more pronounced at O, are found.

The theoretical *ab initio* calculations were carried out according to the SCF–LCAO–MO method (Roothaan, 1951) with the program *BIGMOL* (Thole & van Duijnen, 1971). The clusters WMMW and 1W4M of Fig. 3 were used to simulate the hydrogen bonds in II-*trans-A*.$\frac{1}{2}H_2O$. The geometry of the clusters was deduced from the coordinates obtained by the multipole refinement. H atoms replacing C were placed at the appropriate C—H distance from the C atoms to which they are linked. The GTO basis set (7,3,1/3,1) (Roos & Siegbahn, 1970) was contracted to (4, 2,1/2,1). To study the influence of hydrogen bonding, a

map of type

$$D_{th}(Hb;r) = \rho_{th}(cluster;r) - \rho_{th}(isolated\ mol;r) \quad (3)$$

is also given. The map is not smeared, as this does not provide additional information for the present discussion. On O—H the $D_{th}(Hb;r)$ map (Fig. 4) shows a surplus density, and on O· · ·H a deficiency at H and in the lone-pair region of O. The sharp features at O shown by the theoretical map are not likely to be seen on experimental X–X maps, because of thermal smearing and correlation between sharp deformations and atomic parameters in the HO refinement. The theoretical map does not reveal a tendency for O lone-pair electrons to be polarized towards the hydrogen bond. It cannot be decided yet whether this is due to the quantum-theoretical calculations being based on a molecular cluster rather than on a complete crystal.

The present study shows that further experimental and theoretical work is necessary to obtain conclusive evidence on a possible polarization of the O lone-pair electrons towards the hydrogen bonds. Such studies require extremely accurate atomic parameters, preferably from neutron diffraction work, and quantum-theoretical calculations for extended molecular clusters.

References

COPPENS, P. & VOS, A. (1971). *Acta Cryst.* B27, 146–158.
ROOS, B. & SIEGBAHN, P. (1970). *Theor. Chim. Acta*, 17, 199–208.
ROOTHAAN, C. C. J. (1951). *Rev. Mod. Phys.* 23, 69–89.
STEWART, R. F. (1976). *Acta Cryst.* A32, 565–574.
THOLE, B. T. & VAN DUIJNEN, P.TH. (1971). Chemistry Department, Univ. of Groningen, The Netherlands.
WAL, H. R. VAN DER & VOS, A. (1979a) *Acta Cryst.* B35, 1793–1804.
WAL, H. R. VAN DER & VOS, A. (1979b). *Acta Cryst.* B35, 1804–1809.
WAL, R. J. VAN DER (1982). Thesis, Univ. of Groningen.