

Fig. 2. A perspective drawing of *O*-acetylveramarine and the numbering scheme of the atoms.

what flattened. Ring *B* has a regular cyclohexene half-chair conformation. The five-membered ring *C* has an envelope conformation with C(8) 0.65 Å from the mean plane of the remaining four atoms. Ring *D* adopts a conformation markedly different from that of a normal chair owing to *cis* fusion with ring *C*. This is reflected in the small torsion angles C(13)–C(12)–C(14)–C(15) = –38.6° and C(12)–C(14)–C(15)–C(16) = 40.5°, compared with the value of 56° in cyclohexane. H atoms on the C(16)–OH and C(20)–OH hydroxyl groups are oriented so that they form intramolecular hydrogen bonds: O(2)–H...O(3) and O(3)–H...N(1), with H...O = 2.02 and H...N = 2.19 Å. The crystal structure consists of discrete molecules separated by normal van der Waals contacts.

All calculations were performed on a Siemens 4004/150 computer at the Research Computing Centre

of Comenius University. We are grateful to Dr F. R. Ahmed for kindly supplying us with the NRC system of programs, and Dr J. Soldánová for measurements of intensities on a Syntex *P*2₁ diffractometer.

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Accurate Structure Determination of *trans*-2,5-Dimethyl-3-hexene-2,5-diol Hemihydrate, C₈H₁₆O₂ · ½ H₂O, at 86 K.

I. Results of High-Order and Multipole Refinements

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Abstract

The title compound is orthorhombic, space group *Pbcn*, *Z* = 8, *a* = 9.678 (5), *b* = 10.419 (8), *c* = 18.290 (10) Å at 86 K. Accurate X-ray diffraction intensities were obtained for 9618 independent reflections up to sin θ/λ = 1.08 Å⁻¹, from the intensities measured on a CAD-

4F diffractometer for a complete hemisphere with monochromatized Mo radiation and the step-scan method. Multiple diffraction was avoided on line. A spherical high-order refinement (sin θ/λ > 0.7 Å⁻¹) with scale and overall thermal motion from full-angle data decreased *R_w*(*I*) to 0.108 for the 8255 full-angle and to 0.078 for the 5716 high-order reflections with

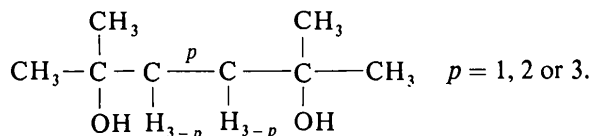
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$w > 0$. The high-order coordinates seem to be affected by bonding effects. Full-angle multipole refinements with up to octopoles on C and O were carried out with the program *VALRAY* with the usual ζ scattering factors (*Z* refinement) and with scattering factors based on the SCF 3P Clementi wave functions for C and O (*P* refinement). $R_w(I)$ dropped to 0.0082 and 0.0081 respectively. The *X*-H distances from these refinements show reasonable agreement with expected values. The multipole scale factors and overall thermal motion turned out to be adjusted predominantly to the high-order data and are thus affected by possible systematic errors in these intensities. Monopole populations for the *Z* refinement agree better with physical concepts than those of the *P* refinement.

1. Introduction

The present paper is part of a series on the electron density distributions on single, double and triple C-C bonds. For the gaseous compounds ethane, ethylene and acetylene at room temperature the electron density distributions have been studied (van Nes, 1978; van Nes & Vos, 1977, 1978, 1979; van Nes & van Bolhuis, 1979). The present investigation of 2,5-dimethyl-3-hexene-2,5-diol is a continuation of the research performed by Ruysink (1973) and Helmholdt (1975) on the (at room temperature) solid compounds.



The accurate X-ray study of deuterated 2,5-dimethyl-3-hexyne-2,5-diol ($p = 3$) has been reported by Helmholdt & Vos (1977). For the compound with $p = 2$, a conventional X-ray study at liquid-nitrogen temperatures by Ruysink & Vos (1974) showed that in crystals which were assumed to contain the *cis* isomer only, *trans* molecules and molecules with $p = 1$ were also present, in total to 33% and in a disordered way. Therefore no further accurate work was planned for these crystals. Also the monoclinic crystals of the pure *trans* compound are not suitable for an accurate determination of the electron density distribution as, according to a recent study by van der Wal & Vos (1979), these crystals show disorder. Therefore for further work on the compound with $p = 2$ the orthorhombic *trans*-2,5-dimethyl-3-hexene-2,5-diol hemihydrate was chosen. This compound will be denoted as II *trans A*. The conventional X-ray study at 113 K published by Ruysink & Vos (1974) reveals that the crystals do not show disorder and that the thermal motion is not too high. The present paper describes the

accurate measurement of the X-ray intensities at 86 K and the results of a spherical high-order refinement and of two full-angle multipole refinements. In the next paper the electron density distribution will be discussed.

2. Preliminary crystallographic work

For growing the crystals the sample obtained from Ruysink (1973) was used. Crystallization took place by slow evaporation of the solvent (6–14 d) from a saturated solution in petroleum ether (40–60°). Large crystals measuring up to $5 \times 2 \times 2$ mm could be grown. In view of the homogeneity region of the X-ray beam, we wanted to obtain spherical crystals with diameters of *ca* 0.5 mm for the X-ray work. To achieve this, a crystal approximately $5 \times 2 \times 1$ mm was cut into pieces of $1 \times 1 \times 1$ mm. These pieces were ground into spheres with approximate diameter 0.7 mm in a cylindrical box of radius 9.5 mm and height 7.5 mm with the cylindrical wall covered with sandpaper. The grinding was done by blowing the crystals along the cylindrical wall by an air stream. A crystal with $\varnothing \approx 0.7$ mm was reduced to $\varnothing \approx 0.5$ mm by dissolving its outer part in petroleum ether (40–60°). This was achieved by putting the crystal into 3 ml of the solvent and stirring crystal plus solvent for about half an hour. The crystals were coated with tixo (a cyanoacrylate-monomer glue which polymerizes rapidly in air) to avoid sublimation, and mounted with tixo on to the top of a glass fiber.

X-ray photographs and diffractometer measurements confirmed the space group determined by Ruysink (1973). Accurate values of the cell dimensions were found by optimizing the θ , ω , κ and φ setting angles of 25 reflections on the CAD-4F diffractometer. The crystal data at 86 K are given in Table 1.

3. Intensity measurements

Set-up of the measurements

The accurate intensity measurements were made on a Nonius CAD-4F diffractometer. In our institute this diffractometer is controlled by a PDP8/M computer equipped with, apart from the RK ϕ 5 disc and tape unit, a floppy disc and a 1200 baud video display. It has therefore been possible to add programs specially designed for the present research (van der Wal & de Boer, 1978) to the standard Nonius CAD-4F system.

Table 1. *Crystal data of $C_8H_{16}O_2 \cdot \frac{1}{2}H_2O$ at 86 K*

Space group: <i>Pbcn</i>	$V = 1844 \text{ \AA}^3$
$a = 9.678 (5) \text{ \AA}$	$Z = 8$
$b = 10.419 (8)$	$D_x = 1.102 \text{ Mg m}^{-3}$
$c = 18.290 (10)$	$\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$
	$\mu(\text{Mo}) = 0.086 \text{ mm}^{-1}$

Care was taken to obtain accurate intensities. The mechanical stability and alignment of the total measurement equipment was checked (for details see van der Wal, 1979). The spherical crystal was kept at a stable temperature of 86 K with the cooling equipment described by van Bolhuis (1971) and van Nes & van Bolhuis (1978), and its adjustment was checked regularly by means of axes matrix control reflections. Mo radiation monochromatized with the device described by Helmholdt & Vos (1977) was used. In the present case a glass fiber was used to flatten the primary X-ray beam (intensity fluctuation $\pm 1.5\%$ over 0.5 mm). The scan speed was chosen such that the measurement of each reflection aimed at a statistical accuracy of 2% in I , but in no case were more than 150 s spent on one reflection intensity.

Multiple reflection was avoided on line. For each reflection \mathbf{H} with $\sin \theta/\lambda < 0.36 \text{ \AA}^{-1}$ a series of three net intensities were measured at ψ values differing by 0.25° , and a least-squares line $I(\mathbf{H}, \psi_i) = a\psi_i + b$ ($i = 1, 3$) was fitted to the data. Multiple reflection was assumed to be absent if the intensities fulfilled the criteria $|a| < 0.1$ and

$$\sum_i [I(\mathbf{H}, \psi_i; \text{obs}) - I(\mathbf{H}, \psi_i; \text{calc})]^2 \leq \sum_i \sigma^2[I(\mathbf{H}, \psi_i)].$$

The first condition was used only to save time; the second condition is the real test on the least-squares line obtained. Measurements not obeying the criteria were rejected, and the measurement was repeated for three different ψ values. The final scan was made at $\psi = \sum_{i=1,3} \psi_i/3$ with ψ_i taken from the ψ set satisfying the criteria. The check was restricted to reflections with low $\sin \theta/\lambda$ values as these reflections are most liable to suffer from multiple reflection (Coppens, 1968). For about 30% of the reflections for which the check was made, more than one set of ψ values had to be used.

All intensities were collected with the step-scan method, and the profiles were analyzed according to method I described by van der Wal, de Boer & Vos (1979). Details are given in Table 2. Some modifications had to be made in the program as, because of the long crystal axes, for $\theta > 25^\circ$ up to three reflections

were recorded in one single profile scan. To this end the two outer parts of the profile, running from steps 1 to $m_L = \text{COG}(\mathbf{H}) - \frac{1}{2}R_g(\mathbf{H})$ and from steps $m_H = \text{COG}(\mathbf{H}) + \frac{1}{2}R_g(\mathbf{H})$ to the end step 96, were smoothed separately (Whittaker & Robinson, 1949, pp. 306–316; $\varepsilon = 0.01$); $\text{COG}(\mathbf{H})$ is the estimated position of the center of gravity of peak \mathbf{H} and $R_g(\mathbf{H})$ the estimated reflection width. Going from m_L and m_H outwards, points n_L and n_H respectively were searched from which on the smoothed profile an intensity increase for three successive steps was observed. The steps $(n_L + 7)$ to $(n_H - 7)$ inclusive were taken as the peak region. The total intensity below the peak was obtained from the intensities $Y(i)$ measured for steps i , as

$$\sum_i Y(i), \quad i = (n_L + 7), (n_H - 7).$$

The total background below the peak was calculated as

$$(n_H - n_L - 13) \left[\sum_i Y(i) + \sum_j Y(j) \right] / 24,$$

$$i = (n_L - 5), (n_L + 6), \quad j = (n_H - 6), (n_H + 5).$$

Intensities of this type have relatively high e.s.d.'s and may also contain systematic errors.

Intensity data

All reflections in one full reciprocal hemisphere up to $\sin \theta/\lambda = 1.08 \text{ \AA}^{-1}$ were collected. In the high-order range ($\sin \theta/\lambda > 0.8 \text{ \AA}^{-1}$), where in nearly all cases the maximum time of 150 s had to be spent on a reflection intensity, each reflection was measured at two very different ψ values to prevent icing and shrinking of the goniometer head. Despite the low temperature (86 K) and the tixo coating of the crystal, slow sublimation of the crystal lowered the intensity of the intensity-control reflections 122; 554 and 458 (measured every hour) by about 1.5% per month or per 5000 profile dumps. Apart from the control reflections, 47 631 profile dumps were recorded and analyzed.

For each set of equivalent reflections (\mathbf{H}, i) the weighted average intensity was calculated as

$$\bar{I}(\mathbf{H}) = \sum_i w(\mathbf{H}, i) I(\mathbf{H}, i) / \sum_i w(\mathbf{H}, i), \quad (1)$$

where $w(\mathbf{H}, i) = 1/\sigma_c^2[I(\mathbf{H}, i)]$ with $\sigma_c[I(\mathbf{H}, i)]$ the e.s.d. based on counting statistics. After this, reflections (\mathbf{H}, i) with

$$|I(\mathbf{H}, i) - \bar{I}(\mathbf{H})| > 3.5[w(\mathbf{H}, i)]^{-1/2} \quad (2)$$

were removed from the reflection list and the average was determined again for the remaining reflections (where necessary this procedure was repeated). In this way 1.3% of the measured intensities were removed from the list. The final averaged intensity was con-

Table 2. Profile analysis data for II trans A

Reflection width $A(\hat{\mathbf{H}}) + B \tan \theta$ *	
Number of directions \mathbf{H}	15
Solid angle around \mathbf{H}	0.23 sr
Minimum number of points per \mathbf{H}	4
Minimum θ spacing per \mathbf{H}	5.7°
Coefficient B constraint to	1.0°
Observed $A(\hat{\mathbf{H}})$ values	0.64–0.77°
SM*	2.7
TH*	0.2

* Method I (van der Wal, de Boer & Vos, 1979).

sidered as the observed intensity $I_o(\mathbf{H})$ for reflection \mathbf{H} . Its e.s.d. was taken as

$$\sigma[I_o(\mathbf{H})] = \left\{ \sum_i [I(\mathbf{H}, i) - \bar{I}(\mathbf{H})]^2 / n(\mathbf{H}) [n(\mathbf{H}) - 1] \right\}^{1/2}, \quad (3)$$

where $n(\mathbf{H})$ is the number of equivalent reflections in set \mathbf{H} . In this way observed intensities and their e.s.d.'s were obtained for 9618 independent reflections. The $|F(\mathbf{H})|^2$ values with e.s.d.'s were calculated by correcting for Lorentz and polarization effects.

4. Spherical refinement

General and low-order refinement

The structure has been discussed by Ruysink & Vos (1974). It consists of layers parallel to the ab plane with thickness of about $0.4c$ (Ruysink & Vos, 1974, Fig. 1). Successive layers lie around $z = \frac{1}{4}$ and $z = \frac{3}{4}$ and are related by the c glide plane perpendicular to \mathbf{b} . Interaction between the layers is by van der Waals forces only. The projection of the layer around $z = \frac{3}{4}$ with the numbering of the atoms is given in Fig. 1. The present numbering scheme differs from that of Ruysink & Vos as follows:

Ruysink & Vos	O(10)	O(11)	C($n + 1$)
Present work	O(2)	O(3)	C(n).

The parameters of Ruysink & Vos were used as starting points for the spherical refinements, which were carried out with XRAY (1976). The function minimized is

$$Q(I) = \sum_{\mathbf{H}} w(\mathbf{H}) [I_o(\mathbf{H}) - K^2 I_c(\mathbf{H})]^2 \quad (4)$$

with

$$w(\mathbf{H}) = 1/\sigma^2[I_o(\mathbf{H})] \quad \text{for } I_o(\mathbf{H}) \geq \sigma[I_o(\mathbf{H})] \quad (5)$$

and

$$w(\mathbf{H}) = 0 \quad \text{for } I_o(\mathbf{H}) < \sigma[I_o(\mathbf{H})].$$

R is defined as

$$R_w(I) = \left\{ \frac{[\sum w(\mathbf{H}) |I_o(\mathbf{H}) - I_c(\mathbf{H})|^2]}{[\sum w(\mathbf{H}) I_o^2(\mathbf{H})]} \right\}^{1/2}. \quad (6)$$

Full-angle (FA), low-order (LO) and high-order (HO) refinements were made; $\sin \theta/\lambda$ ranges with numbers of reflections with $w > 0$ in parentheses are 0–1.08 (8255), 0–0.65 (2028) and 0.7–1.08 \AA^{-1} (5716).

C and O atoms were refined anisotropically. For H the isotropic thermal parameters $B(\mathbf{H})$ and the $X-H$ directions were found from a LO refinement. In all further spherical refinements $B(\mathbf{H})$ and $\mathbf{r}(X-H)$ were

kept fixed with the distances $X-H$ taken as $C(sp^3)-H = 1.08$, $C(sp^2)-H = 1.07$, $(H)O-H = 0.954$, $(R)O-H = 0.97$ \AA (Ellison, Johnson & Levy, 1971; Park, Jeffrey & Hamilton, 1971).

Spherical Sp(FA-HO) refinement

For the calculation of deformation densities, high-order X-ray positional and thermal parameters are generally used if neutron data are not available. However, the scale and overall thermal motion must be determined from the full-angle data to reduce the influence of errors due to thermal diffuse scattering (Kroon & Vos, 1978) and to an incorrect choice of the profile analysis method (van der Wal, de Boer & Vos, 1979) as much as possible. Therefore after the LO refinement a series of alternating FA and HO refinements were made. For FA the scale was varied with all further parameters fixed and for HO positional and thermal parameters were refined with scale fixed and H atoms constrained. The final coordinates for the heavy atoms are listed in Table 3.* For the Sp(FA-HO) parameters $R_w(I)$ is 0.108 for the 8255 FA reflections and 0.078 for the 5716 HO reflections. Geometric data for the molecule and for the hydrogen-bonding system are given in Tables 4 and 5. The values may be compared with the earlier values of Ruysink & Vos (1974) and with the values observed for the monoclinic compound (van der Wal & Vos, 1979) and are not discussed further.

Spherical Sp(HO) refinement

After the Sp(FA-HO) refinement one cycle of HO refinement was carried out, in which the scale and all

* See deposition footnote.

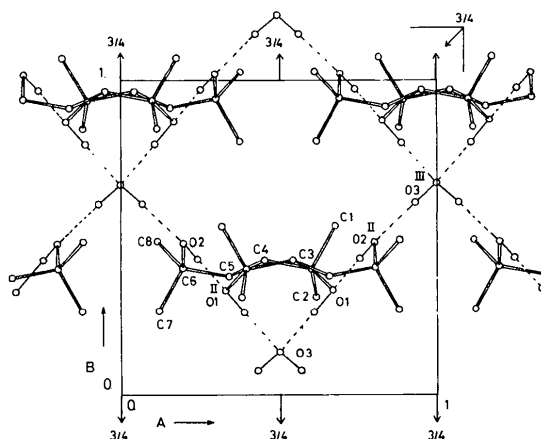


Fig. 1. Projection of the layer around $z = \frac{3}{4}$ along $[001]$ on to the plane (001) . $O^{II} = O(\bar{x} + 1, y, \bar{z} + 1\frac{1}{2})$, $O^{III} = O(x + \frac{1}{2}, y + \frac{1}{2}, \bar{z} + 1\frac{1}{2})$.

Table 3. *Sp(FA-HO) parameters of the heavy atoms*

Numbers in parentheses are the e.s.d.'s in the last digits. Fractional coordinates are multiplied by 10⁵. For numbering see Fig. 1.

	x	y	z
O(1)	66989 (4)	35043 (3)	68357 (2)
C(1)	67940 (5)	54018 (5)	61247 (3)
C(2)	61691 (5)	32959 (6)	55500 (3)
C(3)	60265 (4)	41340 (3)	62278 (2)
C(4)	45489 (4)	43981 (4)	64469 (2)
C(5)	34124 (4)	39176 (4)	61445 (2)
C(6)	19600 (4)	41740 (4)	64172 (2)
C(7)	12146 (5)	29033 (5)	65594 (3)
C(8)	11750 (5)	49744 (6)	58544 (3)
O(2)	19827 (4)	49161 (3)	70740 (2)
O(3)	50000 (-)	16481 (5)	75000 (-)

Table 4. *Geometric data calculated from the Sp(FA-HO) parameters*

E.s.d.'s of all distances are smaller than 0.75×10^{-3} Å, and of all angles not involving H smaller than 0.04° .

Bond lengths (Å)			
C(4)–C(5)	1.3290	C=C	1.3290
C(4)–C(3)	1.5105		
C(5)–C(6)	1.5152	$\langle C(sp^2)–C(sp^3) \rangle$	1.5129
C(3)–C(2)	1.5227		
C(3)–C(1)	1.5271		
C(6)–C(8)	1.5272		
C(6)–C(7)	1.5300	$\langle C(sp^3)–C(sp^3) \rangle$	1.5268
C(6)–O(2)	1.4288		
C(3)–O(1)	1.4457	$\langle C(sp^3)–O \rangle$	1.4373
Angles (°)			
O(1)–C(3)–C(1)	105.58	O(2)–C(6)–C(8)	106.19
O(1)–C(3)–C(2)	108.97	O(2)–C(6)–C(7)	109.43
O(1)–C(3)–C(4)	107.75	O(2)–C(6)–C(5)	110.97
C(1)–C(3)–C(2)	110.57	C(8)–C(6)–C(7)	110.64
C(1)–C(3)–C(4)	109.61	C(8)–C(6)–C(5)	109.63
C(2)–C(3)–C(4)	113.97	C(7)–C(6)–C(5)	109.93
C(5)–C(4)–C(3)	127.19	C(4)–C(5)–C(6)	124.36
C(5)–C(4)–H(8)	119.27	C(4)–C(5)–H(9)	120.93
C(3)–C(4)–H(8)	113.49	C(6)–C(5)–H(9)	114.72

Equation of the C(3)C(4)C(5) plane (**X**, **Y** and **Z** are orthonormal axes parallel to **a**, **b** and **c**), and distances of atoms to the plane (Å)

$$0.0303X - 0.7702Y + 0.6371Z = 4.116 \text{ Å}$$

O(1) 1.234; C(1) -1.115; C(2) -0.113; C(3) 0; C(4) 0; C(5) 0; C(6) 0.069; C(7) 1.233; C(8) -1.252; O(2) 0.240

heavy-atom parameters were varied. The coordinates of the heavy atoms changed by 0.2σ on average, while the average change in U_{ii} was -0.00044 Å^2 [about $4\sigma(U_{ii})$]. The scale factor decreased considerably, from 1.214 to 1.182. The larger part of the decrease is accounted for by the decrease in thermal parameters. In the present case an increase in HO intensities caused by the neglect of thermal diffuse scattering errors may partly be balanced by a decrease in the intensities due to the overlap of the reflection profiles.

5. Multipole refinements

Multipole functions

The data have been subjected to a valence analysis according to Stewart (1976). After some modifications (van der Wal, 1979) the program VALRAY (Stewart, 1974) was used for the refinements. For each pseudo atom p with nuclear position \mathbf{R}_p the density is given by

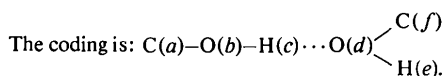
$$\begin{aligned} \rho_p(\mathbf{r}_p) = & \text{Pop}_p(\text{core}) \rho_p(\text{core}, \mathbf{r}_p) \\ & + \sum_l \sum_{m=0}^l C_p^e(l, m) \text{Pop}_p^e(l, m) \rho_p(l, \mathbf{r}_p) \\ & \times P_l^m(\cos \theta_p) \cos m\varphi_p + \sum_l \sum_{m=1}^l C_p^o(l, m) \\ & \times \text{Pop}_p^o(l, m) \rho_p(l, \mathbf{r}_p) P_l^m(\cos \theta_p) \sin m\varphi_p, \quad (7) \end{aligned}$$

with $\mathbf{r}_p = \mathbf{r} - \mathbf{R}_p$; $\rho_p(\text{core}, \mathbf{r}_p)$ and $\rho_p(l, \mathbf{r}_p)$ are normalized radial density functions. $P_l^m(\cos \theta_p) \cos m\varphi_p$ and $P_l^m(\cos \theta_p) \sin m\varphi_p$ are associated Legendre functions; r_p , θ_p and φ_p are polar coordinates corresponding to \mathbf{r}_p . The normalization constants $C_p^e(l, m)$ and $C_p^o(l, m)$ are chosen so as to satisfy the conditions

$$C_p^e(0, 0) \int \rho_p(0, \mathbf{r}_p) d\mathbf{r} = 1 \quad (8)$$

$$C_p^e(l, m) \int |\rho_p(l, \mathbf{r}_p) P_l^m(\cos \theta_p) \cos m\varphi_p| d\mathbf{r}_p = 2 \quad (9)$$

and similarly for $C_p^o(l, m)$. The latter equation implies that $\text{Pop}_p^e(l, m)$ and $\text{Pop}_p^o(l, m)$ give the number of electrons transferred from the negative to the positive

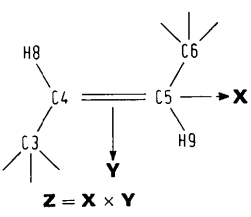
Table 5. *Distances (Å) and angles (°) for the hydrogen bridges in II trans A*

In bridges where the water molecule takes part, C(a) and C(f) are replaced by H(a) and H(f), respectively. Standard deviations for distances and angles not involving hydrogen atoms are 0.6×10^{-3} Å for O···O and 0.03° for C–O···O.

b	d	b–d	c–d	b–c–d	a–b–c	a–b–d	e–d–f	b–d–e	b–d–f
O(3 ^{III})	O(2 ^{II})	2.747	1.799	172.35	103.50	100.53	110.16	116.50	125.68
O(2 ^{II})	O(1)	2.787	1.818	177.98	110.16	108.84	109.39	113.08	121.12
O(1)	O(3)	2.814	1.849	173.37	109.39	112.39	103.50	132.54	100.07

part of the multipole function. The choice of the reference frame is given in Table 6. The orientation of the frame relative to the crystal axes, as determined after the Sp(FA-HO) refinement, did not require readjustment during the multipole refinement as the changes in the coordinates were only small (Tables 3 and 8). The multipole functions applied and the nomenclature for the populations used in Table 8, are listed in Table 7. The large number of refineable populations was slightly reduced in the following way. (a) For C(4) and C(5) local symmetry m was assumed, m coinciding with the plane C(3)–C(4)–C(5). This means that for both C(4) and C(5) six parameters $D3$, $Q3$, $Q4$, $O3$, $O4$ and $O7$ are set to zero. (b) For O(3) of the water molecule, lying on the twofold axis, the seven refineable multipole parameters were not considered and only the monopole population was refined.

Table 6. Choice of reference frame $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ for II trans A , and its orientation with respect to the crystal system



Direction cosines			
	a	b	c
X	-0.82804	-0.37696	-0.41683
Y	0.55978	-0.51616	-0.65076
Z	0.03019	-0.76892	0.64088

Table 7. Associated Legendre functions normalized according to equations (8) and (9), expressed in the direction cosines q_x , q_y and q_z of \mathbf{r}_p with respect to the reference frame \mathbf{X}, \mathbf{Y} and \mathbf{Z}

Dipole		
$C^e(1,1)\text{Pop}^e(1,1)P_1^1(\cos \theta) \cos \varphi = 4$	$\times D1 \times$	q_x
$C^o(1,1)\text{Pop}^o(1,1)P_1^1(\cos \theta) \cos \varphi = 4$	$\times D2 \times$	q_y
$C(1,0)\text{Pop}(1,0)P_1^0(\cos \theta) = 4$	$\times D3 \times$	q_z
Quadrupole		
$C^e(2,2)\text{Pop}^e(2,2)P_2^2(\cos \theta) \cos 2\varphi = \pi/2$	$\times Q1 \times$	$3(q_x^2 - q_y^2)$
$C^o(2,2)\text{Pop}^o(2,2)P_2^2(\cos \theta) \sin 2\varphi = \pi/2$	$\times Q2 \times$	$6(q_x q_y)$
$C^e(2,1)\text{Pop}^e(2,1)P_2^1(\cos \theta) \cos \varphi = \pi$	$\times Q3 \times$	$3(q_x q_z)$
$C^o(2,1)\text{Pop}^o(2,1)P_2^1(\cos \theta) \sin \varphi = \pi$	$\times Q4 \times$	$3(q_y q_z)$
$C(2,0)\text{Pop}(2,0)P_2^0(\cos \theta) = 3\sqrt{3}$	$\times Q5 \times$	$3(q_z^2 - \frac{1}{3})/2$
Octopole		
$C^e(3,3)\text{Pop}^e(3,3)P_3^3(\cos \theta) \cos 3\varphi = 16/45$	$\times O1 \times$	$15(q_x^2 - 3q_y^2) q_x$
$C^o(3,3)\text{Pop}^o(3,3)P_3^3(\cos \theta) \sin 3\varphi = 16/45$	$\times O2 \times$	$15(3q_x^2 - q_y^2) q_y$
$C^e(3,2)\text{Pop}^e(3,2)P_3^2(\cos \theta) \cos 2\varphi = 4\pi/15$	$\times O3 \times$	$15(q_x^2 - q_y^2) q_z$
$C^o(3,2)\text{Pop}^o(3,2)P_3^2(\cos \theta) \sin 2\varphi = 4\pi/15$	$\times O4 \times$	$30(q_x q_y q_z)$
$C^e(3,1)\text{Pop}^e(3,1)P_3^1(\cos \theta) \cos \varphi = \frac{8\pi}{3} \left(\tan^{-1} 2 + \frac{14}{5} - \frac{\pi}{4} \right)^{-1}$	$\times O5 \times$	$3(5q_z^2 - 1)q_x/2$
$C^o(3,1)\text{Pop}^o(3,1)P_3^1(\cos \theta) \sin \varphi = \frac{8\pi}{3} \left(\tan^{-1} 2 + \frac{14}{5} - \frac{\pi}{4} \right)^{-1}$	$\times O6 \times$	$3(5q_z^2 - 1)q_y/2$
$C(3,0)\text{Pop}(3,0)P_3^0(\cos \theta) = 40/7$	$\times O7 \times$	$(5q_z^2 - 3)q_z/2$

Scattering factors for C and O

The scattering factors are given by

$$f_p(\mathbf{S}) = \text{Pop}_p(\text{core}) f_p(\text{core}, \mathbf{S}) + \sum_l \sum_{m=0}^l C_p^e(l, m) \times \text{Pop}_p^e(l, m) i^l f_p(l, \mathbf{S}) P_l^m(\cos \theta_S) \cos m\varphi_S + \sum_l \sum_{m=1}^l C_p^o(l, m) \text{Pop}_p^o(l, m) i^l f_p(l, \mathbf{S}) \times P_l^m(\cos \theta_S) \sin m\varphi_S, \quad (10)$$

with $f_p(l, \mathbf{S})$ the Fourier Bessel transform of $\rho(l, r_p)$,

$$f_p(l, \mathbf{S}) = 4\pi \int_0^\infty \rho_p(l, r_p) j_l(Sr_p) r_p^2 dr_p; \quad (11)$$

$j_l(Sr_p)$ is an l th order spherical Bessel function. For the C and O cores the scattering factors were derived from the SCF(3P) wave functions of Clementi (1965). For the valence electrons two types of scattering factors were applied, resulting in two types of refinement.

(a) Refinements with adjustable ζ (Z refinements): the $f(Z)$ scattering factors [except that for O(3) whose monopole was treated according to b)] were obtained from the single exponential radial function

$$\rho_{p, n_p}(r_p) = (4\pi)^{-1} [(2\zeta_p)^{n_p+3}/(n_p+2)!] r_p^{n_p} \exp[-2\zeta_p r_p]. \quad (12)$$

The integers n_p were chosen as 2, 2, 2, 3, 4 for the monopoles, dipoles, quadrupoles, octopoles and hexadecapoles respectively. The ζ values were adjusted during the refinements.

(b) Refinements with SCF scattering factors (P refinements): fixed scattering-factor curves $f(P)$

Table 8. *Final parameters for the Z and P refinements; positional and thermal parameters are multiplied by 10⁵*

For numbering scheme see Fig. 1. A hyphen means constraint. $R_w(I; Z) = 0.0082$, $R_w(I; P) = 0.0081$. The temperature factor is defined as $T(hkl) = \exp[-2\pi^2(U_{11}h^2 a^{*2} + U_{22}k^2 b^{*2} + U_{33}l^2 c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	Z	P	Z	P	Z	P	Z	P
	O(1)		C(1)		C(2)		C(3)	
ζ	2.209 (4)		1.620 (13)		1.633 (13)		1.630 (7)	
x	66995 (4)	66980 (3)	67937 (4)	67935 (4)	61697 (4)	61697 (4)	60255 (3)	60258 (3)
y	35042 (3)	35041 (3)	54003 (4)	54003 (4)	32961 (5)	32964 (4)	41345 (3)	41348 (3)
z	68349 (2)	68350 (2)	61242 (3)	61242 (3)	55500 (2)	55504 (2)	62282 (2)	62277 (2)
U_{11}	983 (10)	1057 (10)	1281 (14)	1298 (13)	1365 (13)	1390 (12)	837 (9)	862 (8)
U_{22}	1363 (9)	1464 (10)	1527 (16)	1570 (9)	2083 (14)	2097 (14)	1179 (9)	1215 (8)
U_{33}	1120 (9)	1205 (9)	2078 (16)	2101 (15)	1307 (13)	1337 (13)	1034 (9)	1067 (9)
U_{12}	34 (8)	62 (9)	-265 (9)	-253 (9)	390 (10)	400 (10)	23 (8)	35 (8)
U_{13}	-150 (8)	-155 (8)	52 (12)	54 (12)	125 (10)	111 (9)	40 (8)	35 (8)
U_{23}	230 (10)	209 (10)	596 (11)	582 (11)	-230 (12)	-211 (12)	111 (8)	133 (8)
Pop(core)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)
Pop(0,0)	6.09 (3)	6.30 (2)	4.00 (11)	4.40 (3)	3.91 (10)	4.47 (3)	3.87 (4)	4.32 (2)
$D1$	-0.051 (9)	-0.115 (8)	-0.014 (15)	-0.042 (15)	-0.014 (15)	0.027 (15)	0.021 (9)	0.021 (8)
$D2$	-0.008 (7)	0.015 (7)	-0.045 (16)	-0.065 (17)	0.012 (13)	0.050 (11)	0.071 (9)	0.049 (8)
$D3$	0.009 (9)	-0.021 (10)	0.021 (15)	0.018 (14)	0.012 (17)	-0.000 (16)	-0.039 (9)	-0.035 (8)
$Q1$	-0.035 (8)	-0.058 (8)	-0.026 (11)	-0.047 (11)	0.018 (10)	0.040 (10)	-0.010 (9)	-0.010 (9)
$Q2$	0.047 (8)	0.047 (8)	0.027 (15)	0.037 (16)	-0.007 (12)	-0.017 (12)	0.021 (9)	0.002 (8)
$Q3$	0.016 (9)	-0.019 (9)	0.011 (12)	0.002 (11)	-0.009 (14)	-0.025 (14)	0.074 (9)	0.066 (9)
$Q4$	0.010 (8)	0.033 (8)	-0.002 (10)	-0.008 (10)	0.036 (9)	0.054 (9)	-0.001 (9)	0.001 (8)
$Q5$	-0.107 (9)	-0.149 (10)	-0.018 (14)	-0.002 (14)	-0.018 (13)	0.017 (13)	-0.041 (9)	-0.045 (9)
$O1$	0.012 (7)	0.013 (6)	-0.102 (16)	-0.115 (10)	-0.146 (13)	-0.158 (9)	0.142 (10)	0.169 (8)
$O2$	-0.014 (7)	-0.021 (7)	-0.026 (12)	-0.019 (10)	-0.071 (11)	-0.065 (10)	0.056 (10)	0.043 (8)
$O3$	-0.005 (7)	-0.003 (7)	-0.061 (10)	-0.059 (9)	0.020 (11)	0.014 (10)	0.002 (10)	-0.013 (9)
$O4$	0.012 (7)	0.002 (7)	-0.022 (11)	-0.011 (10)	0.008 (12)	-0.000 (10)	0.023 (10)	0.020 (9)
$O5$	-0.081 (11)	-0.062 (11)	-0.326 (25)	-0.307 (15)	-0.181 (27)	-0.242 (16)	0.271 (16)	0.331 (13)
$O6$	0.005 (10)	0.006 (10)	-0.028 (17)	-0.024 (15)	-0.059 (16)	-0.057 (15)	0.026 (14)	0.022 (13)
$O7$	0.007 (9)	0.002 (8)	0.079 (15)	0.078 (12)	0.034 (14)	0.045 (12)	-0.017 (11)	-0.031 (10)
	C(4)		C(5)		C(6)		C(7)	
ζ	1.578 (3)		1.624 (3)		1.615 (6)		1.654 (15)	
x	45498 (3)	45498 (3)	34111 (3)	34109 (3)	19602 (3)	19605 (3)	12138 (4)	12140 (4)
y	43981 (3)	43979 (3)	39172 (3)	39176 (3)	41743 (3)	41741 (3)	29032 (4)	29039 (4)
z	64471 (2)	64470 (2)	61439 (2)	61439 (2)	64170 (2)	64169 (2)	65591 (3)	65589 (3)
U_{11}	774 (10)	816 (10)	864 (10)	904 (9)	825 (9)	896 (9)	1517 (14)	1528 (13)
U_{22}	1137 (9)	1170 (8)	1208 (9)	1227 (9)	1136 (9)	1160 (8)	1521 (14)	1544 (13)
U_{33}	1040 (10)	1063 (9)	1024 (9)	1042 (9)	1073 (10)	1086 (10)	1965 (17)	1986 (15)
U_{12}	13 (7)	14 (7)	63 (8)	60 (7)	70 (7)	67 (7)	-445 (10)	-434 (9)
U_{13}	-44 (8)	-48 (8)	-20 (8)	-15 (8)	-25 (8)	-26 (8)	135 (12)	140 (12)
U_{23}	-95 (8)	-96 (8)	-208 (9)	-212 (9)	-58 (9)	-65 (8)	-167 (13)	-166 (12)
Pop(core)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)
Pop(0,0)	4.32 (7)	4.42 (2)	3.94 (7)	4.40 (3)	4.01 (4)	4.28 (2)	3.71 (12)	4.41 (3)
$D1$	0.067 (13)	0.048 (11)	-0.024 (13)	-0.039 (12)	0.023 (9)	0.033 (8)	0.010 (16)	0.030 (15)
$D2$	0.017 (13)	0.016 (12)	-0.043 (12)	-0.015 (11)	0.015 (8)	0.011 (8)	0.036 (16)	0.032 (17)
$D3$	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	0.023 (10)	0.015 (9)	-0.041 (16)	0.001 (14)
$Q1$	0.084 (12)	0.079 (16)	0.017 (11)	0.018 (10)	0.002 (8)	-0.008 (8)	0.006 (11)	-0.006 (11)
$Q2$	-0.004 (12)	0.007 (11)	0.034 (12)	0.055 (12)	-0.049 (8)	-0.037 (8)	0.040 (15)	0.037 (15)
$Q3$	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	0.023 (9)	0.022 (9)	0.029 (13)	0.005 (12)
$Q4$	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	0.019 (8)	0.014 (8)	0.013 (10)	0.012 (10)
$Q5$	-0.184 (13)	-0.171 (10)	-0.159 (13)	-0.204 (10)	0.033 (10)	0.034 (10)	0.001 (14)	-0.013 (14)
$O1$	-0.238 (16)	-0.210 (10)	0.195 (15)	0.208 (10)	-0.182 (10)	-0.201 (9)	0.102 (15)	0.122 (10)
$O2$	-0.070 (13)	-0.053 (11)	0.036 (13)	0.035 (11)	-0.013 (9)	-0.007 (8)	-0.017 (12)	-0.012 (10)
$O3$	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	0.009 (9)	0.002 (8)	0.078 (11)	0.060 (10)
$O4$	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	-0.043 (10)	-0.047 (9)	0.048 (12)	0.051 (10)
$O5$	-0.118 (16)	-0.098 (14)	0.087 (15)	0.095 (14)	-0.321 (17)	-0.315 (13)	0.228 (25)	0.271 (15)
$O6$	0.036 (14)	0.024 (12)	-0.015 (14)	-0.003 (13)	0.020 (14)	0.006 (13)	0.037 (17)	0.037 (16)
$O7$	0.000 (-)	0.000 (-)	0.000 (-)	0.000 (-)	0.054 (12)	0.063 (11)	-0.023 (15)	-0.035 (13)

Table 8 (cont.)

	Z	P	Z	P
	C(8)		O(2)	
ζ	1.610 (13)		2.215 (5)	
x	11749 (5)	11754 (4)	19836 (4)	19835 (3)
y	49741 (5)	49738 (4)	49156 (4)	49151 (3)
z	58554 (3)	58552 (2)	70738 (4)	70742 (2)
U_{11}	1285 (13)	1315 (12)	1072 (10)	1111 (10)
U_{22}	2208 (15)	2230 (14)	1297 (11)	1393 (11)
U_{33}	1499 (14)	1524 (13)	1170 (12)	1291 (11)
U_{12}	391 (11)	385 (11)	305 (9)	308 (9)
U_{13}	-311 (11)	-313 (10)	73 (9)	95 (9)
U_{23}	161 (12)	157 (12)	-216 (10)	-245 (10)
Pop(core)	2.00 (-)	2.00 (-)	2.00 (-)	2.00 (-)
Pop(0,0)	4.05 (11)	4.39 (3)	6.08 (3)	6.33 (2)
$D1$	0.052 (16)	0.071 (16)	0.022 (8)	0.041 (9)
$D2$	0.101 (16)	0.100 (16)	-0.070 (7)	-0.082 (7)
$D3$	0.045 (16)	0.043 (14)	-0.038 (11)	-0.096 (11)
$Q1$	-0.019 (11)	-0.017 (11)	0.008 (8)	-0.002 (8)
$Q2$	0.090 (15)	0.097 (15)	-0.089 (8)	-0.129 (8)
$Q3$	-0.030 (14)	-0.025 (13)	0.067 (9)	0.109 (9)
$Q4$	-0.012 (10)	-0.009 (10)	0.014 (8)	0.034 (9)
$Q5$	-0.059 (13)	-0.072 (13)	0.014 (10)	-0.038 (10)
$O1$	0.093 (15)	0.101 (10)	0.027 (7)	0.033 (6)
$O2$	-0.029 (12)	-0.025 (10)	-0.017 (7)	-0.017 (7)
$O3$	-0.045 (11)	-0.037 (9)	-0.015 (7)	-0.007 (7)
$O4$	0.065 (14)	0.069 (11)	0.007 (7)	0.012 (7)
$O5$	0.218 (24)	0.214 (16)	0.051 (12)	0.033 (11)
$O6$	-0.027 (16)	-0.032 (15)	0.026 (10)	0.017 (10)
$O7$	-0.067 (14)	-0.079 (13)	-0.022 (9)	-0.026 (8)
	O(3)			
x	50000	50000		
y	16495 (3)	16501 (3)		
z	75000	75000		
U_{11}	1334 (11)	1330 (11)		
U_{22}	988 (8)	978 (8)		
U_{33}	1641 (12)	1639 (12)		
U_{12}	0	0		
U_{13}	-408 (9)	-410 (9)		
U_{23}	0	0		
Pop(core)	2.00 (-)	2.00 (-)		
Pop(0,0)	6.41 (2)	6.45 (2)		

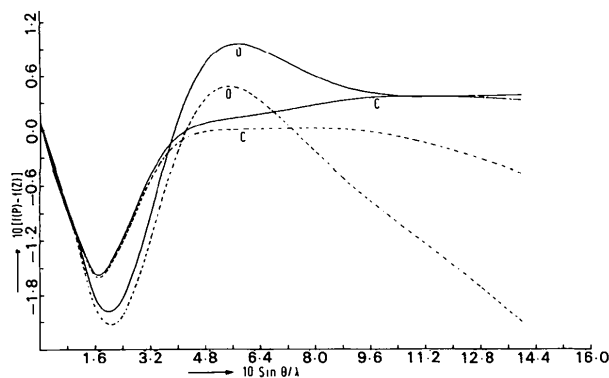


Fig. 2. $f(P) - f(Z)$ curves for C and O, with $f(Z)$ based on formula (12) with $\zeta(C) = 1.61$, $\zeta(O) = 2.21$ a.u. Full lines represent static atoms; dashed lines account for the difference in thermal parameters for the P and Z refinements (equation 14).

derived from Clementi's $3P$ wave functions were applied for monopoles and multipoles up to the quadrupole level. The octopole scattering factor was calculated from (10) and (11) with $\zeta(C) = 1.72$ and $\zeta(O) = 2.25$ a.u. [standard molecular values obtained by energy minimization for atoms in molecules (Hehre, Stewart & Pople, 1969)].

In Fig. 2 the differences $f(P) - f(Z)$ for the monopole scattering factors are given for C and O. In both cases in the high-order range $f(P) > f(Z)$, implying that $\rho(r, P)$ has more inner-shell character than $\rho(r, Z)$. In the low-order range $f(P) < f(Z)$.

Polarized H atoms

We have applied the *VALRAY* option of the so-called polarized H atoms. This implies that for H, in addition to a monopole with variable population, one dipole function is considered which is kept adjusted in the $X-H$ direction. The atom has a fixed population LSH for the dipole and fixed radial scattering factors. The monopole and dipole scattering factors were taken from Stewart, Bentley & Goodman (1975). For the dipole population LSH, with scaling according to (9), the value 0.25 was used.

Refinement procedure and results

All refinements were based on intensities. The function minimized and the weighting scheme are as given by (4) and (5), except for the fact that $w = 0$ is taken for the reflections with $|F_o(\mathbf{H})| < 2\sigma[|F_o(\mathbf{H})|]$. 8553 independent reflections with $0 < \sin \theta/\lambda < 1.08 \text{ \AA}^{-1}$ were taken into account. The atomic vibrations were assumed to be linear and harmonic. Extinction was not considered, as preliminary multipole refinements gave an extinction parameter which was either negative or not significantly different from zero. We have fixed the core populations of C and O at 2. During the refinement of the populations the program *VALRAY* refers the scale factor K to the core populations only and considers the quantities $K \text{Pop}(l, m)$ for the populations of the valence electrons. The sum of the monopole populations is not constrained to the total number of electrons. From the populations $\text{Pop}(l, m)$ given in Tables 8 and 9, populations normalized to the total number of electrons n can be obtained by multiplying all monopole populations by a factor η such that

$$\eta \left[\sum_p \text{Pop}_p(\text{core}) + \sum_p \text{Pop}(0,0) \right] = n. \quad (13)$$

At the same time the scale factor must be corrected to $K(\text{corr}) = K/\eta$.

In total we refined, in addition to the scale factor, 84 positional parameters, 81 thermal parameters and 178

Table 9. Final parameters of the *Z* and *P* refinement for the H atoms

The positional parameters are multiplied by 10^5 . B (\AA^2) is from the temperature factor $\exp[-B(\sin^2 \theta/\lambda^2)]$.

	<i>Z</i>	<i>P</i>	<i>Z</i>	<i>P</i>
	H(1)		H(9)	
<i>x</i>	60384 (93)	61072 (80)	34677 (49)	34640 (50)
<i>y</i>	27934 (94)	28489 (82)	33060 (50)	32886 (49)
<i>z</i>	70280 (39)	70152 (36)	56695 (31)	56490 (30)
<i>B</i>	2.9 (2)	2.9 (2)	2.6 (2)	1.8 (2)
Pop(0,0)	0.88 (3)	1.04 (3)	1.07 (2)	0.93 (1)
	H(2)		H(10)	
<i>x</i>	78598 (153)	78625 (122)	17326 (94)	17562 (85)
<i>y</i>	52047 (69)	52097 (65)	23712 (92)	23474 (79)
<i>z</i>	60298 (40)	60309 (39)	69615 (62)	69805 (53)
<i>B</i>	2.6 (2)	2.6 (2)	3.1 (2)	2.7 (2)
Pop(0,0)	1.03 (4)	1.03 (3)	1.19 (5)	1.03 (3)
	H(3)		H(11)	
<i>x</i>	66902 (74)	66868 (71)	11757 (73)	11715 (72)
<i>y</i>	60061 (106)	60245 (86)	23495 (100)	23317 (85)
<i>z</i>	66106 (78)	66207 (62)	60666 (78)	60561 (63)
<i>B</i>	2.4 (2)	2.4 (2)	3.32 (2)	3.2 (2)
Pop(0,0)	0.95 (4)	0.91 (3)	1.09 (5)	1.01 (3)
	H(4)		H(12)	
<i>x</i>	63717 (90)	63761 (82)	2205 (147)	1875 (118)
<i>y</i>	59011 (98)	58931 (84)	30900 (63)	30959 (62)
<i>z</i>	56609 (73)	56641 (61)	67235 (42)	67281 (39)
<i>B</i>	3.2 (2)	3.5 (2)	3.0 (2)	2.8 (2)
Pop(0,0)	1.05 (5)	1.09 (3)	1.18 (5)	1.08 (3)
	H(5)		H(13)	
<i>x</i>	56575 (92)	56476 (80)	11362 (74)	11364 (70)
<i>y</i>	24129 (122)	23876 (97)	44320 (92)	44242 (78)
<i>z</i>	56255 (37)	56250 (36)	53075 (82)	53027 (62)
<i>B</i>	2.9 (2)	2.4 (2)	2.0 (2)	2.1 (2)
Pop(0,0)	1.11 (5)	1.02 (3)	0.81 (4)	0.84 (3)
	H(6)		H(14)	
<i>x</i>	57341 (85)	57296 (78)	1576 (144)	1500 (120)
<i>y</i>	37581 (80)	37748 (72)	51152 (65)	51082 (62)
<i>z</i>	50838 (68)	50592 (56)	60276 (39)	60295 (37)
<i>B</i>	2.8 (2)	2.4 (2)	2.7 (2)	2.9 (2)
Pop(0,0)	1.09 (4)	0.98 (3)	1.10 (5)	1.11 (3)
	H(7)		H(15)	
<i>x</i>	72516 (136)	72688 (111)	16474 (91)	16485 (30)
<i>y</i>	31283 (62)	31253 (60)	58456 (126)	58494 (101)
<i>z</i>	54426 (36)	54414 (35)	57782 (40)	57723 (38)
<i>B</i>	2.3 (2)	2.4 (2)	2.6 (2)	2.7 (2)
Pop(0,0)	1.01 (4)	0.99 (3)	1.11 (5)	1.14 (4)
	H(8)		H(16)	
<i>x</i>	44418 (50)	44518 (48)	24605 (79)	24177 (69)
<i>y</i>	50091 (46)	50089 (43)	43674 (77)	44227 (66)
<i>z</i>	69302 (30)	69307 (28)	74826 (54)	74620 (48)
<i>B</i>	1.5 (1)	1.5 (1)	2.8 (2)	2.4 (2)
Pop(0,0)	0.92 (1)	0.93 (1)	0.91 (3)	0.98 (2)
			H(17)	
		<i>x</i>	42747 (64)	42798 (62)
		<i>y</i>	10394 (60)	10460 (60)
		<i>z</i>	72876 (30)	72868 (29)
		<i>B</i>	2.8 (2)	2.8 (2)
		Pop(0,0)	0.87 (2)	0.88 (2)

population parameters. Moreover in the ζ refinements ten ζ values were adjusted. $R_w(I)$ decreased to 0.0082 for the *Z* and to 0.0081 for the *P* refinement. The final parameters are listed in Tables 8 and 9.* Geometrical data are given in Tables 10 and 11.

6. Discussion of the multipole refinement results

Comparison of the heavy-atom parameters

Apart from the O(1) positions which show a difference of 0.0015 \AA , all corresponding coordinates of the *Z* and *P* refinements are equal within 2σ . Therefore the bond lengths and angles in Table 11 have been calculated for the average atomic positions. Also equal values are found for the non-monopole populations. The monopole parameters depend, however, on the type of scattering factor. As would be expected from the difference in scattering factors (solid lines in Fig. 2), for *P* the U_{ii} values are larger than for *Z*. Average values for ΔU_{ii} are $\langle \Delta U_{ii}(C) \rangle = 0.00026$, $\langle \Delta U_{ii}(O) \rangle = 0.00085 \text{ \AA}^2$. The relatively large increase for O is due to the fact that $f(P) - f(Z)$ is larger for O than for C in the HO region. After correction of $f(P)$ for the difference in thermal parameters by taking

$$f_{\text{corr}}(P) = f(P) \exp(-8\pi^2 \langle \Delta U_{ii} \rangle \sin^2 \theta / \lambda^2), \quad (14)$$

the dashed lines $f_{\text{corr}}(P) - f(Z)$ of Fig. 2 are obtained. For C, where $f_{\text{corr}}(P) - f(Z)$ is predominantly negative in the region where the valence electrons

* Lists of observed and calculated intensities of the *Z* multipole refinement, anisotropic thermal parameters of the heavy atoms and positional and thermal parameters of the H atoms after the Sp(FA-HO) refinement of § 4, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34359 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 10. C-H distances (\AA)

The e.s.d. is about 0.01 \AA for all distances.

	<i>Z</i>	<i>P</i>	<i>Z</i>	<i>P</i>
C(4)-H(8)	1.09	1.09	C(1)-H(2)	1.07
C(5)-H(9)	1.08	1.12	C(1)-H(3)	1.09
Mean <i>Z/P</i>	1.085	1.105	C(1)-H(4)	1.07
Mean <i>Z + P</i>	1.095		C(2)-H(5)	1.05
Lit. (§ 4)	1.07		C(2)-H(6)	1.06
			C(2)-H(7)	1.08
O(1)-H(1)	1.05	0.95	C(7)-H(10)	1.05
O(2)-H(16)	1.05	0.97	C(7)-H(11)	1.07
Mean <i>Z/P</i>	1.050	0.960	C(7)-H(12)	1.03
Mean <i>Z + P</i>	1.005		C(8)-H(13)	1.15
Lit. (§ 4)	0.97		C(8)-H(14)	1.04
			C(8)-H(15)	1.03
O(3)*-H(17)	1.02	1.02	Mean <i>Z/P</i>	1.066
Mean <i>Z + P</i>	1.020		Mean <i>Z + P</i>	1.076
Lit. (§ 4)	0.95		Lit. (§ 4)	1.08

* No multipoles on O(3).

contribute (up to $\sin \theta/\lambda \simeq 0.6 \text{ \AA}^{-1}$), the average $P(0,0)$ values are 0.41 larger for P than for Z . For O, where both negative and positive $f_{\text{corr}}(P) - f(Z)$ values occur in the region of the valence electrons (up to $\sin \theta/\lambda \simeq 0.75 \text{ \AA}^{-1}$), the average increase in $\text{Pop}(0,0)$ is only 0.23.

In comparison with the total number of electrons n , the sum of the monopole populations is only 0.67% too high for the Z refinement. For P this value is 4.6%. Normalization of the P monopole populations would therefore reduce the core populations to the unrealistic value of 1.91. That not much physical significance can be attached to the P populations is also seen from the fact that the normalized values give on average a surplus population of 0.10 e on C, and a deficit of 0.08 e on O. For Z the reverse situation occurs, C has a deficit of 0.08 e and O a surplus of 0.04 e, in agreement with chemical intuition.

Hydrogen parameters

Although for the two types of refinement the same scattering factors have been used for H, corresponding H atom parameters are not equal, evidently due to correlation with the heavy atoms. For H atoms linked to C the P refinement $\text{Pop}(0,0)$ values tend to be lower than for Z , in agreement with the fact that for P the C

populations are relatively high. For H atoms linked to O a slight reverse trend is observed. Not only the populations, but also the H atom positions are unequal for the two cases. This is seen from Table 10 where the C—H and O—H distances are given. Corresponding thermal parameters $B(H)$ of the two refinements do not differ much and decrease in the order: $B(H;HC=CH) < B(H,CH_3) < B(H,OH)$.

Table 10 shows that the use of the polarized H atoms has given (average) X —H distances close to the expected values. The only exceptions are the (C)O—H distances for the Z refinement where the dipole effect seems to have been overestimated by the applied LSH value.

ζ values

Because of the correlation of ζ with $\text{Pop}(0,0)$ apparent from the final parameters in Table 8, no useful trend concerning the radial functions of chemically inequivalent C or O atoms can be deduced from the ζ values. The average $\zeta(C)$ and $\zeta(O)$ values of 1.61 and 2.21 a.u. respectively may be compared with energy-minimized values $\zeta(C) = 1.72$, $\zeta(O) = 2.25$ (Hehre, Stewart & Pople, 1969) and with the density-minimized values $\zeta(C) = 1.52$, $\zeta(O) = 2.22$ (Bentley & Stewart, 1976) for atoms in molecules. It should be noted that the energy-minimized values tend to be higher than the density-minimized values as energy minimization tends to concentrate the electrons around the nuclei. The two theoretical ζ values for O do not differ much and the present $\zeta(O)$ value shows reasonably good agreement with theory. The present value for C, 1.61, lies closer to the density-minimized value than the value of 1.69 a.u. obtained for C_2H_2 and C_2H_4 by van Nes (1978). Further experimental average ζ values are $\zeta(C) = 1.60$, $\zeta(O) = 2.08$ for 1,1'-azobis-carbamide (Cromer, Larson & Stewart, 1976); $\zeta(C) = 1.58$ for diamond (Stewart, 1973); $\zeta(C) = 1.63$ for melamine (Cromer, Larson & Stewart, 1976).

Table 11. Geometric data calculated from the average parameters of the multipole refinements

For numbering see Fig. 1. E.s.d.'s of all distances are smaller than 0.75×10^{-3} , and of all angles not involving H smaller than 0.04° .

Bond lengths (Å)			
C(4)—C(5)	1.3315	C=C	1.3315
C(4)—C(3)	1.5086	$\langle C(sp^2)-C(sp^3) \rangle$	1.5113
C(5)—C(6)	1.5140		
C(3)—C(2)	1.5228		
C(3)—C(1)	1.5256		
C(6)—C(8)	1.5255	$\langle C(sp^3)-C(sp^3) \rangle$	1.5261
C(6)—C(7)	1.5304		
C(6)—O(2)	1.4286	$\langle C(sp^3)-O \rangle$	1.4369
C(3)—O(1)	1.4452		
Angles ($^\circ$)			
O(1)—C(3)—C(1)	105.60	O(2)—C(6)—C(8)	106.20
O(1)—C(3)—C(2)	108.86	O(2)—C(6)—C(7)	109.40
O(1)—C(3)—C(4)	107.78	O(2)—C(6)—C(5)	111.00
C(1)—C(3)—C(2)	110.48	C(8)—C(6)—C(7)	110.59
C(1)—C(3)—C(4)	109.70	C(8)—C(6)—C(5)	109.66
C(2)—C(3)—C(4)	114.03	C(7)—C(6)—C(5)	109.63
C(5)—C(4)—C(3)	127.21	C(4)—C(5)—C(6)	124.32
C(5)—C(4)—H(8)	118.68	C(4)—C(5)—H(9)	121.15
C(3)—C(4)—H(8)	114.00	C(6)—C(5)—H(9)	114.52

Equation of the C(3)C(4)C(5) plane (X , Y and Z are orthonormal axes parallel to a , b and c) and distances of atoms to the plane (Å)

$$0.0303X - 0.7710Y + 0.6361Z = 4.102 \text{ \AA}$$

O(1) 1.232; C(1) -1.115; C(2) -0.111; C(3) 0; C(4) 0; C(5) 0; C(6) 0.069; C(7) 1.233; C(8) -1.250; O(2) 0.239

7. Multipole and high-order refinement results

Molecular geometry

Comparison of the coordinates in Tables 8 and 3 shows that, relative to the multipole refinement position, in the $\text{Sp}(\text{FA}-\text{HO})$ refinement O(1) is shifted by 0.0014 \AA towards the lone-pair region. The shift makes an angle of 47° with the C—O bond direction (expected value about 55°). For O(2) the corresponding values are 0.0011 \AA and 66° . This indicates that in the spherical $\text{Sp}(\text{FA}-\text{HO})$ refinement the O atoms still try to compensate the influence of the lone pairs. The O atom shifts are of the same order as the shifts observed for the C=O oxygen atoms in cyanuric

acid (Coppens & Vos, 1971). In the latter compound for a high-order refinement ($\sin \theta/\lambda > 0.65 \text{ \AA}^{-1}$) the O atoms shift on average 0.004 \AA from their neutron diffraction position towards the lone-pair region.

From the bond lengths in Tables 11 and 4 we see that corresponding C–O lengths are practically equal for the two types of refinement, implying that the C atoms attached to O tend to follow the HO shift of O atoms. Further the tables show that the HO value for C=C is 0.0025 \AA smaller than the multipole value. Evidently the unequal bonding effects for the double and single C–C bonds still influence the HO positions for C. The increase of the HO values for the C–C single bonds, in comparison with the multipole refinement values, can be explained by the HO shift for C–O and the HO shortening of C=C. On the basis of these effects the average increase for C–C is estimated at 0.0011 \AA for C(sp^2)–C(sp^3) and at 0.0004 \AA for C(sp^3)–C(sp^3), in good agreement with the increases deduced from the bond lengths obtained from the refinements.

Thermal parameters and scale factors

In Table 12 the scale factors and the $\langle U_{ii} \rangle$ values of the spherical refinements Sp(FA–HO) and Sp(HO) are compared with the scale factors and the $\langle U_{ii} \rangle$ values of the multipole Z and P refinements. The Sp(HO) and P refinements, which both make use of the 3P atomic scattering factors, show reasonably good agreement for the scale and temperature-factor parameters. This means that in the present FA multipole refinements, the thermal parameters and the scale factor are determined mainly by the HO data.

8. Conclusions

The multipole refinements have given excellent agreement between observed and calculated intensities as can be seen from the low value of 0.0082 for $R_w(I)$. However, due to correlation with the scale factor and the type of radial function used, the populations do not have a physical meaning. Scale and overall thermal motion are determined predominantly by the HO

intensities, and are therefore affected by the systematic errors occurring especially in the HO data due to, for instance, TDS and possible imperfections in the profile analysis method (van der Wal, de Boer & Vos, 1979). Better extrapolation to $F(000)$, necessary for the determination of a correct scale, can possibly be achieved by use of more flexible radial distribution functions as applied, for instance, in the so-called κ refinements. Research to improve the radial functions is in progress. Thermal diffuse scattering has not yet been corrected for, as the elastic constants are not known, whereas the formalism developed by Kroon (1977) for rigid bodies is not applicable because of the non-rigid character of the molecules.

The small differences between the HO and multipole coordinates indicate that bonding effects still influence the reflections with $\sin \theta/\lambda > 0.7 \text{ \AA}^{-1}$ to some extent. A careful neutron diffraction study is necessary to check whether the multipole refinement coordinates represent the nuclear positions best.

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Table 12. Scale factors and $\langle U_{ii} \rangle$ values (in 10^{-5} \AA^2) from spherical and multipole refinements

For nomenclature see the text. In the calculation of the $\langle U_{ii}(\text{O}) \rangle$ values the water oxygen is not considered.

	Sp(FA–HO)	Sp(HO)		P	Z
<i>K</i>	1.214	1.182	<i>K</i>	1.176	1.180
$\langle U_{ii}(\text{C}) \rangle$	1412	1367	$\langle U_{ii}(\text{C}) \rangle$	1350	1324
$\langle U_{ii}(\text{O}) \rangle$	1303	1260	$\langle U_{ii}(\text{O}) \rangle$	1253	1168

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Accurate Structure Determination of *trans*-2,5-Dimethyl-3-hexene-2,5-diol Hemihydrate, $C_8H_{16}O_2 \cdot \frac{1}{2}H_2O$, at 86 K.

II. Discussion of the Electron Density Distribution

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Abstract

Experimental deformation densities for the title compound are compared with a smeared theoretical deformation density based on *ab initio* quantum-chemical calculations for a model compound (9,5,1/5,2 GTO basis set). Around the C–C bonds in the ethylene plane very good agreement with theory is obtained for the experimental $D(HO, \mathbf{r})$ map. This map is based on high-order parameters of a conventional X-ray refinement, but with scale and overall thermal motion adjusted to full-angle data. Around the O atoms where $D(HO, \mathbf{r})$ is not reliable, the theoretical map is compared with a multipole map not including monopole deformations and based on a multipole refinement with ζ scattering factors. The multipole map clearly shows the influence of the hydrogen bonds on the deformation density.

1. Introduction

In the previous paper (van der Wal & Vos, 1979; hereafter WV) the parameters obtained for the title compound by high-order X-ray refinement and multipole refinement have been discussed. In the present

paper the deformations in the electron density due to chemical bonding (bonding effects) are reported and compared with the bonding effects expected on the basis of quantum chemical calculations. The compound $C_8H_{16}O_2 \cdot \frac{1}{2}H_2O$ will be referred to as II *trans A*.

2. Experimental density distributions

Deformation density $D(HO, \mathbf{r})$

The observed deformation-density distribution is defined as

$$\begin{aligned}
 D(\mathbf{r}) &= Sc^{-1} \rho_o(\mathbf{r}) - \rho_c(\text{atoms}; \mathbf{r}) \\
 &= \sum_{\mathbf{H}} [Sc^{-1} F_o(\mathbf{H}) - F_c(\text{atoms}; \mathbf{H})] \\
 &\quad \times \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}); \quad (1)
 \end{aligned}$$

$\rho_c(\text{atoms}; \mathbf{r})$ is based on spherically symmetric non-bonded atoms, Sc is the scale factor. The map has been calculated with the scale, positional and thermal parameters from the Sp(FA–HO) refinement discussed in WV. This implies that scale and overall thermal motion are adjusted to the full-angle data, whereas the