

A Neutron Diffraction Refinement of the Crystal Structure of Erythritol at 22.6 K†

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Abstract

Erythritol, 1,2,3,4-butanetetrol (R^*,S^*), CAS No. 31904-60-6, $C_4H_{10}O_4$, $M_r = 122.08$, $I4_1/a$, $a = 12.713$ (5), $c = 6.747$ (2) Å at 22.6 K, $Z = 4$, $D_c = 1.487$ Mg m⁻³, molecular symmetry $\bar{1}$. The structure has been refined with 1077 neutron diffraction data measured at 22.6 K to an $R(F^2)$ of 0.041. The molecules in the crystal have orientational disorder about the C(2)–O(2) bond with H(O2) having 15% occupancy of an alternate site. Rigid-body analyses, based on the non-hydrogen atoms and on all atoms except the hydroxyl H atoms gave excellent fits, with r.m.s. ΔU_{ij} 's of 0.0004 and 0.0006 Å² respectively. The bond lengths corrected for librational motion are C(1)–C(2), 1.524 (1); C(2)–C(2'), 1.541 (1); C(1)–O(1), 1.427 (1); C(2)–O(2), 1.435 (1) Å. The bond lengths corrected for riding motion are C(1)–H(C11), 1.114 (1); C(1)–H(C12), 1.116 (1); C(2)–H(C2), 1.117 (1); O(1)–H(O1), 0.999 (1); O(2)–H(O2), 0.985 (1); O(2)–H(O2)*, 0.923 (1) Å. The H...O hydrogen-bond lengths and O–H...O angles (uncorrected) are 1.699 (2) Å, 173.3 (2)°; 1.788 (2) Å, 164.5 (2)°. The shorter O(1)–H...O(1) bonds form infinite helical chains about the 4₁ axes; the longer O(2)–H...O(2) bonds form closed quadrilaterals about the 4 axes. The minor components of the disordered H atom form the same quadrilaterals about the 4 axes in the opposite direction.

Introduction

Erythritol is the *meso* isomer of the two tetrityls. The crystals have been studied by several investigators (Jaeger & Haga, 1916; Burgers, 1926; Schönfeldt, Herrmann & Hassel, 1926; Powell, 1956; Shimada, 1958; Bekoe & Powell, 1959), the last of whom determined the crystal structure, with the exception of

the H atom positions, from two-dimensional X-ray data. There is a preliminary report of a neutron diffraction study at room temperature by Shimada *et al.* (1975), but no details of these results have been published.

This neutron study at 22.6 K is aimed at providing precise experimental molecular and crystal structural dimensions for eventual comparison with *ab initio* quantum-mechanical calculations.

Experimental

A crystal of volume 8.6 mm³ with faces {110}, {201} was obtained by slow evaporation from a 50–50 ethanol–water solution. It was mounted parallel to [110] on a hollow aluminum pin. The neutron diffraction data were collected with a closed-cycle helium refrigerator* mounted on an automated four-circle diffractometer at the Brookhaven High-Flux Beam Reactor. A beryllium (002) crystal monochromator was used to obtain a neutron beam of wavelength 1.0445 (1) Å [based upon KBr, $a_0 = 6.6000$ (13) Å at 298 K]. The temperature for the duration of the experiment was 22.6 ± 0.5 K. Calibration of the platinum resistance thermometer was based on the magnetic transition of FeF₂. The cell dimensions and their standard deviations were obtained by least-squares refinement based upon the 2θ values of 64 reflections ($39^\circ < 2\theta < 50^\circ$). Reflection intensities were measured in one octant of reciprocal space for $2\theta < 105^\circ$ using a $\theta/2\theta$ step scan. Scan widths were determined from the relation $\Delta 2\theta = 0.60^\circ + 4.31^\circ \tan \theta$ for the high-angle data ($50^\circ < 2\theta < 105^\circ$) and were held fixed at 3.0° for the low-angle data ($2\theta < 50^\circ$). The step size was adjusted to permit between 59 and 90 steps per scan. The intensities of two reflections, monitored every 50 measurements, did not vary significantly during the course of the experiment. The intensity data were corrected for absorption using an analytical procedure (de Meulenaer & Tompa, 1965;

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* DISPLEX® Model CS-202, Air Products & Chemicals Inc.

Templeton & Templeton, 1973). With $\mu = 0.291 \text{ mm}^{-1}$ (using $\mu_m = 2.39 \text{ m}^2 \text{ kg}^{-1}$ for H), the maximum and minimum absorption corrections were 1.933 and 1.567, respectively.

The starting atomic positional parameters of C and O were taken from Bekoe & Powell (1959) with an assumed uniform isotropic thermal parameter $U = 0.019 \text{ \AA}^2$. The difference Fourier synthesis computed with this model revealed positions for the five H atoms in the asymmetric unit. Refinement of the structure parameters was by full-matrix least-squares minimization of the quantity $\sum w(|F_o|^2 - |F_c|^2)^2$ taking $w^{-1} = \sigma_c^2 + (0.02F^2)^2$, where σ_c^2 is the variance derived from counting statistics. The neutron coherent scattering amplitudes (fm), -3.74 for H, 6.65 for C, 5.803 for O, were taken from Koester (1977). The parameters varied in the latter stages of the refinement included one scale factor, the atomic positional and thermal parameters and the anisotropic extinction parameters for a type I crystal with a Lorentzian distribution of mosaicity (Becker & Coppens, 1975). The indices of fit at convergence for the 1077 recorded observations were $R(F^2) = 0.055$, $R_w(F^2) = 0.073$, $S = 1.96$, values which were less satisfactory than expected. Examination of a ΔF map revealed that the structure model was incomplete; an alternate position with a scattering density of -2.85σ was found for the H atom attached to O(2). Site-occupancy factors at the alternate H-atom positions were varied together with parameters of the types listed above; the sum of the two occupancies was 1.035 (13) at convergence; $R(F^2) = 0.041$, $R_w(F^2) = 0.050$, $S = 1.33$. In later refinements, this sum was constrained to be unity. The extinction corrections were changed little by the change in the structure model. There were 38 reflections for which corrections Y ($Y.F_o^2$) were less than 0.6, with the smallest being 0.31 for 220. Omission of these reflections from the refinement produced no significant

change in the structure parameters, the largest being 0.38σ (U_{33}) for H(O2), although the scale changed by 1.8σ and an extinction component by as much as 3.6σ . The fit was improved somewhat: $R(F^2) = 0.039$, $R_w(F^2) = 0.048$, $S = 1.23$.

The reported parameters, given in Table 1, are derived from the entire data set. The final indices of fit are $R(F^2) = 0.041$, $R_w(F^2) = 0.050$, $S = 1.34$. On the final ΔF map the largest error was $|\Delta e| = 0.51\sigma(e)$, where $\sigma(e) = 0.079 \times 10^{-14} \text{ m \AA}^{-3}$, as computed by the method of Cruickshank (1965). The molecular dimensions and their e.s.d.'s, computed from the variance-covariance matrix (Busing, Martin & Levy, 1964), are given in Table 2. The thermal ellipsoids are shown in Fig. 1. Fig. 2 shows the crystal structure viewed down the c axis.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35594 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

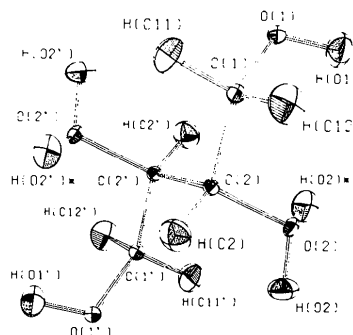


Fig. 1. Erythritol at 22.6 K. The thermal ellipsoids are at 60% probability (Johnson, 1976). The primed and unprimed atoms are related by the center of symmetry. The * refers to the minority component of the H(O2) disordered atoms.

Table 1. Fractional atomic coordinates and anisotropic temperature factors ($\times 10^4$), and occupancy factors and extinction parameters for erythritol

The temperature-factor expression used is $T(H) = \exp[-2\pi^2(h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23})]$. Estimated standard deviations given in parentheses refer to the least significant digit.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Occupancy factors
C(1)	-369 (0)	-737 (0)	2448 (1)	65 (2)	57 (2)	53 (2)	0 (2)	-1 (2)	6 (2)	
C(2)	212 (0)	13 (0)	1068 (1)	45 (2)	49 (2)	52 (2)	1 (2)	-1 (2)	-1 (2)	
O(1)	-1467 (0)	-520 (0)	2534 (1)	59 (2)	75 (3)	78 (3)	-10 (2)	6 (2)	-12 (2)	
O(2)	105 (1)	1054 (0)	1861 (1)	86 (3)	47 (2)	67 (2)	-5 (2)	-2 (2)	-13 (2)	
H(C11)	-277 (1)	-1548 (1)	1919 (2)	238 (6)	115 (5)	248 (6)	10 (4)	33 (5)	-18 (4)	
H(C12)	-19 (1)	-685 (1)	3934 (2)	209 (6)	261 (6)	122 (5)	-5 (4)	-43 (4)	18 (4)	
H(C2)	1049 (1)	-215 (1)	1061 (2)	122 (5)	200 (5)	190 (5)	20 (4)	-1 (4)	-7 (4)	
H(O1)	-1603 (1)	73 (1)	3434 (2)	186 (5)	175 (5)	209 (5)	18 (4)	11 (4)	-67 (4)	
H(O2)	670 (1)	1505 (1)	1407 (2)	142 (6)	138 (6)	239 (7)	-54 (5)	34 (5)	-2 (5)	0.85
H(O2)*	-488 (8)	1390 (8)	1477 (16)	248 (47)	217 (40)	325 (48)	-37 (41)	83 (39)	-120 (36)	0.15

Anisotropic extinction parameters ($\times 10^{-1} \text{ rad}^{-1}$)

g_{11}	43 (2)	g_{22}	31 (2)	g_{33}	25 (2)	g_{12}	-10 (1)	g_{13}	25 (2)	g_{23}	2 (1)
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Table 2. *Molecular dimensions of erythritol at 22.6 K*

The corrected C—C and C—O bond lengths were based on the heavy-atom model (r.m.s. $\Delta U_{ij} = 0.0004 \text{ \AA}^2$). The C—H and O—H corrections were for riding motion only. Primed coordinates are related to the corresponding unprimed coordinates by a center of symmetry.

Bond lengths (Å)		Observed	Corrected
C(1)—C(2)		1.523 (1)	1.524
C(2)—C(2')		1.539 (1)	1.541
C(1)—O(1)		1.425 (1)	1.427
C(2)—O(2)		1.433 (1)	1.435
C(1)—H(C11)		1.097 (1)	1.114
C(1)—H(C12)		1.099 (1)	1.116
C(2)—H(C2)		1.104 (1)	1.117
O(1)—H(O1)		0.983 (1)	0.999
O(2)—H(O2)		0.969 (1)	0.985
O(2)—H(O2)*		0.905 (1)	0.923

Valence angles (°)			
C(1)—C(2)—C(2')	112.9 (1)	H(C11)—C(1)—H(C12)	108.1 (1)
O(2)—C(2)—C(2')	109.7 (1)	C(1)—O(1)—H(O1)	110.3 (1)
O(1)—C(1)—C(2)	112.2 (1)	C(2)—O(2)—H(O2)	111.0 (1)
H(C2)—C(2)—C(2')	109.1 (1)	H(C11)—C(1)—C(2)	109.8 (1)
H(C2)—C(2)—O(2)	109.6 (1)	H(C12)—C(1)—C(2)	108.9 (1)
O(1)—C(1)—H(C11)	107.4 (1)	O(1)—C(1)—H(C12)	110.3 (1)
O(2)—C(2)—C(1)	107.7 (1)	H(C2)—C(2)—C(1)	107.8 (1)
		C(2)—O(2)—H(O2)*	114.1 (6)

Torsion angles (°)			
C(1)—C(2)—O(2)—H(O2)	+156.2 (1)		
C(1)—C(2)—O(2)—H(O2)*	−86.3 (7)		
C(1)—C(2)—C(2')—O(2')	−59.9 (1)		
C(1)—C(2)—C(2')—H(C2')	+60.2 (1)		
C(2)—C(1)—O(1)—H(O1)	−80.2 (1)		
C(2)—C(2')—C(1')—O(1')	+58.4 (1)		
C(2)—C(2')—C(1')—H(C11')	−61.1 (1)		
C(2)—C(2')—C(1')—H(C12')	−179.2 (1)		
C(2)—C(2')—O(2')—H(O2')	+80.5 (1)		
C(2)—C(2')—O(2')—H(O2)*	+37.0 (7)		
O(1)—C(1)—C(2)—O(2)	+62.9 (1)		
O(1)—C(1)—C(2)—H(C2)	−178.9 (1)		
O(2)—C(2)—C(1)—H(C11)	−177.7 (1)		
O(2)—C(2)—C(1)—H(C12)	−59.5 (1)		
O(2)—C(2)—C(2')—H(C2')	−59.9 (1)		
H(C11)—C(1)—C(2)—H(C2)	−59.5 (1)		
H(C11)—C(1)—O(1)—H(O1)	+159.0 (1)		
H(C12)—C(1)—C(2)—H(C2)	+58.7 (1)		
H(C12)—C(1)—O(1)—H(O1)	+41.4 (1)		
H(C2)—C(2)—O(2)—H(O2)	+39.2 (1)		
H(C2)—C(2)—O(2)—H(O2)*	+156.7 (7)		

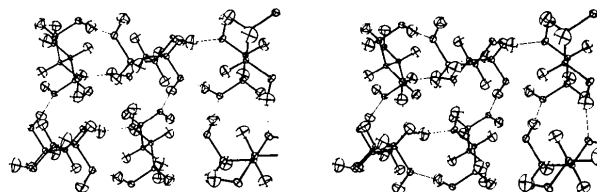


Fig. 2. Stereoview of the crystal structure of erythritol at 22.6 K. The single lines are hydrogen bonds. The minority components H(O2)* have been omitted for clarity. They form hydrogen bonds around the 4 axes in the opposite direction from the majority components.

Table 3. *Least-squares fit to the rigid-body motion for erythritol*

First model excludes the H atoms; second model excludes H(O1), H(O2) and H(O2)*, and includes other H atoms with modified ellipsoids as described in the text.

	First model	Second model
R.m.s. $U_{ij} - U_{ij,r.b.m.}$	0.00038 Å ²	0.00055 Å ²
Max $ U_{ij} - U_{ij,r.b.m.} $	0.00094	0.00210
$\sigma(U_{ij})$	0.00054	0.00065

	First model		Second model		
	T (Å ² × 10 ⁴)	ω (deg ²)	T (Å ² × 10 ⁴)	ω (deg ²)	Direction relative to axes
T (Å ² × 10 ⁴)	42 (4)	5 (4) −6 (3)	45 (4)	3 (3) −6 (3)	
		41 (4) −3 (3)		37 (3) −5 (3)	
		53 (3)		52 (3)	
ω (deg ²)	1.9 (6)	0.9 (6) −1.2 (6)	2.6 (4)	0.5 (4) −1.2 (4)	
		2.2 (6) −0.7 (4)		1.8 (4) −0.4 (3)	
		4.1 (10)		3.9 (7)	

	Tensor	R.m.s. values	Direction relative to axes		
			<i>a</i>	<i>b</i>	<i>c</i>
First model	T	0.076 Å	64.4°	73.2°	148.7°
		0.066	56.2	48.7	59.7
		0.060	44.8	133.9	82.8
	ω	2.2°	64.6	70.3	146.9
		1.5	67.6	39.4	59.5
		1.0	35.1	122.5	78.3
Second model	T	0.075 Å	61.3	74.7	146.8
		0.065	30.2	88.7	59.8
		0.060	81.3	164.7	102.5
	ω	2.2°	59.5	79.6	147.4
		1.4	49.6	55.6	59.2
		1.2	55.4	143.7	80.2

The thermal-motion analysis

The thermal motion was modelled with the segmented-body-analysis program *ORSBA* (Johnson, 1970*a,b*). Two models were considered: one in which the rigid body was composed of the heavy atoms only and a second in which the rigid body was composed of all but the hydroxyl H atoms. For the second model, the values for the mean-square displacements of the H atoms due to the internal modes of motion were obtained as follows. The C—H mean-square stretch displacement was assumed to be 0.0058 Å² which is the spectroscopic value for methane (Cyvin, 1968). The H-atom displacements, orthogonal to the C—H bond

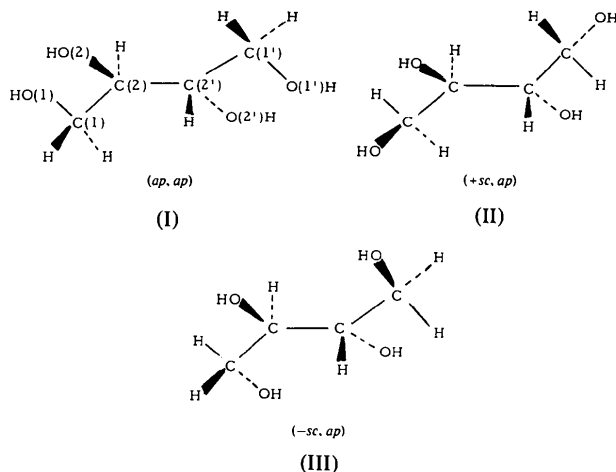
direction (due to scissoring and wagging motion), were computed with *ORSBA*. These correspond to the half-diameters of the central section through the ellipsoid normal to the C—H bond direction. The resultant values, 0.0164 and 0.0129 Å², were in good agreement with the (symmetric) spectroscopic value for methane of 0.0155 Å². The assumed and computed mean-square internal displacements were then subtracted from the thermal-motion ellipsoids of the H atoms prior to the rigid-body fitting.

The rigid-body analysis of the first model resulted in a r.m.s. ΔU_{ij} of 0.00038 Å²; that for the second model

was 0.00055 \AA^2 . The results are given in Table 3. The difference between the two models for **T** and **ω** was not large, as seen in Table 3. Furthermore, the bond-length and valence-angle corrections (involving those atoms common to both rigid bodies, *i.e.* the heavy atoms) were identical for both models. The bond lengths involving H were corrected for riding motion (Busing & Levy, 1964); these are given in Table 2. They differ from those computed with the 'ride-on-rigid' formulation (Johnson, 1970*b*) by no more than 0.002 \AA (1σ).

Discussion

Three staggered centrosymmetrical conformations, (I), (II), and (III), are possible for the erythritol molecule, of which (I) is fully extended and (II) and (III) are bent with respect to the C—C and terminal C—O bonds. The conformation observed is (II), as shown in Fig. 1. The Klyne & Prelog (1960) notation refers to the orientation of the C—C bonds and the terminal O—H bonds.



As with the primary alcohol group in aldohexopyranose sugars, conformations (I) and (II) would be expected to occur, with approximately equal probability, in aqueous solution or in the crystalline state (*cf.* Jeffrey & French, 1978; Marchessault & Perez, 1979). Conformation (III), on the other hand, is expected to be the most stable conformation for isolated or gas-phase molecules, due to its potential for formation of an intramolecular hydrogen bond between the syndiaxially oriented hydroxyl groups. In the crystalline state, intermolecular hydrogen bonding generally takes precedence over intramolecular bonding, as in this structure. Conformational polymorphism could therefore occur, but, as is the case with the higher homologues of the polyols (Jeffrey & Kim, 1970), it has not been reported for the tetrityls.

The bond orientation about the central bond of the molecule is the ideal staggered arrangement, with the

torsion angles about C(2)—C(2') differing from 60° by less than 2σ . The orientation about C(1)—C(2) is less ideal, with angles of 58 and 63° , see Table 2. This is not unexpected, since C(2) is an asymmetrical C atom and the non-bonding intramolecular environment of O(2), for example, is asymmetrical. There is orientational disorder about the C(2)—O(2) bond, so that H(O2) occupies two of the three possible staggered positions in the ratio 85 : 15.

The two C—C bond lengths are significantly different, by 0.016 \AA [observed (8σ); 0.017 \AA corrected], that in the center of the molecule being the longer. The difference in the two C—O bond lengths is smaller, 0.008 \AA (4σ), and its significance is less certain. The observed C(2)—H bond is 0.006 \AA longer than the mean of the two C(1)—H bonds, but this difference is reduced to 0.002 \AA (less than 2σ) by the riding-motion corrections. We conclude, therefore, that all the C—H bond lengths are equal, with a mean corrected value of $1.116 (1) \text{ \AA}$. This is in excellent agreement with the results of room-temperature neutron diffraction studies of glycolic acid (Ellison, Johnson & Levy, 1971) and α -D-glucose (Brown & Levy, 1979), where segmented-body models (Johnson, 1970*a,b*) were also used for the thermal-motion analyses. These analyses gave corrected C—H distances between $1.115 (3)$ and $1.118 (3) \text{ \AA}$ for glycolic acid and between $1.112 (4)$ and $1.127 (3) \text{ \AA}$ for α -D-glucose. These values are significantly longer than the theoretical and experimental spectroscopic values for the C—H bonds in methane and methanol which are in the range of 1.081 to 1.097 \AA (Pople, 1977; DeFrees, Levi, Pollack, Hehre, Binkley & Pople, 1979) and are closer to the uncorrected mean value at 23 K of 1.100 \AA .

The observed primary and secondary alcohol O—H bond lengths differ by 0.014 \AA (10σ); this is unchanged by the riding-motion correction. These values are longer than the theoretical and experimental values for methanol of 0.970 and $0.963 (8) \text{ \AA}$, but the difference is smaller than for the C—H bonds. Similar discrepancies between crystallographic and theoretical C—H and N—H bond lengths were found from the comparison of low-temperature neutron diffraction results and *ab initio* MO calculations on acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980).

The hydrogen bonding shown in Fig. 2 is as inferred from the X-ray analysis (Bekoe & Powell, 1959). It consists of infinite spirals linking the O(1) atoms about the 4_1 axes, and quadrilaterals that are almost squares linking the O(2) atoms about the $\bar{4}$ axes. As predicted from consideration of the 'cooperative effect' (see Jeffrey, Gress & Takagi, 1977; Tse & Newton, 1977), the bonds involved in the infinite chains are shorter than those in the finite chains.

The details of the hydrogen-bond geometry are shown in Fig. 3. The small departure from linearity of O(1)—H...O(1') is such that the H atom is closer to

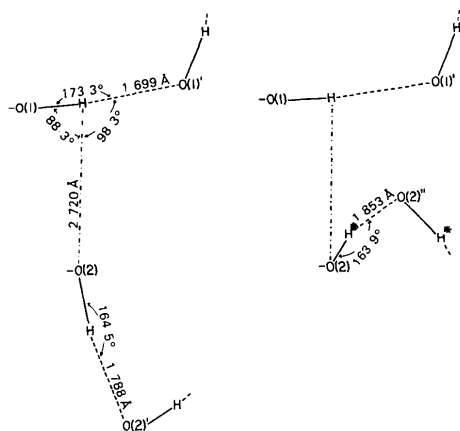


Fig. 3. The hydrogen-bond geometry in the crystal structure of erythritol at 22.6 K. The e.s.d.'s for the distances are 0.003 Å, for the angles 0.3°, except for those involving H* where they are 0.02 Å and 0.7°.

O(2) of the same molecule than it otherwise would be had the bond been linear, and the H atom is in the plane of the three O atoms, indicating an intramolecular attraction. Although the $H \cdots O(2)$ distance is less than the sum of the Pauling (1960) values for the van der Waals radii, 2.80 Å, we doubt whether we should describe this as an *unsymmetrical bifurcated* hydrogen bond, as observed in β -L-lyxopyranose (Nordenson, Takagi & Jeffrey, 1978) and in some other carbohydrate crystals (Jeffrey, 1979). The $O(2)-H \cdots O(2')$ is further from linearity, but in that case the closest next-neighbor O to the H atom is another O(2) at 2.964 Å. The minor component $O(2)-H^* \cdots O(2')$ forms the same quadrilateral in the opposite sense about the $\bar{4}$ axis. The observed covalent $O(1)-H^*$ bond length is anomalously short, and has large thermal parameters. If it is corrected to 0.97 Å, the $H(O2)^* \cdots O$ hydrogen-bond length is equal to that of the major component within the experimental error.

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