

Thiamin Pyrophosphate. $4\frac{1}{2}\text{H}_2\text{O}$: A Second Polymorph of the Neutral Zwitterion

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Abstract

The molecular structure and crystal packing for this polymorph of cocarboxylase are very similar to those of the tetrahydrate, although it contains an additional half molecule of water per formula unit and only one formula unit per asymmetric unit. The colorless tabular crystals of $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_7\text{P}_2\text{S}\cdot 4\frac{1}{2}\text{H}_2\text{O}$ are triclinic with $Z = 2$. The crystal structure was determined with diffractometer data obtained by the θ - 2θ scan technique (Cu radiation) from a crystal with space group $P\bar{1}$ ($P1$) and unit-cell parameters $a = 13.445$ (1), $b = 12.418$ (1), $c = 6.981$ (1) Å, $\alpha = 74.18$ (1), $\beta = 99.55$ (1) and $\gamma = 105.59$ (1)°. The structure was refined by blocked least-squares calculations to $R = 0.049$ for the 3349 observed reflections and $R = 0.050$ for all 3524 reflections.

Experimental

The crystallization of thiamin pyrophosphate, TPP, as a neutral zwitterion produced two polymorphic forms as described in the paper on the prismatic form (Pletcher, Wood, Blank, Shin & Sax, 1977). The colorless tabular crystals, which are the subject of this paper, were also triclinic as indicated by Weissenberg photographs and were assumed to have $P\bar{1}$ space-group symmetry. Cell parameters and intensity data were measured on a crystal mounted on a fiber parallel to the b axis. The crystal plate was 0.08 mm thick along a , 0.31 mm along b and 0.24 mm along c with approximately $\frac{1}{4}$ of the nearly rectangular plate cut away by the formation of a (011) face. The cell parameters were determined (Picker FACS-1 Disk Operating System, 1972) from a least-squares fit of the setting angles for 12 centered reflections (setting angles for each reflection were averages of the four values obtained at $\pm 2\theta$, χ and $\pm 2\theta$, $180 + \chi$; 2θ ranged from 44 to 75°). The cell parameters and other crystal data are given in Table 1. For collection of the intensity data, the crystal was coated with mineral oil to retard loss of water of crystallization even though there were no indications of the instability observed with the first polymorph. The

intensity data were collected on a Picker FACS-1 system using the θ - 2θ scan technique over a range of 2.4° at a scan rate of 2° min⁻¹ with graphite-monochromated ($2\theta_m = 26.14^\circ$) Cu radiation to a 2θ limit of 127.5°. Background counts were accumulated for 20 s at either end of the scan range. The intensities of three standard reflections, which were monitored after every 50 reflections, exhibited fluctuations that did not exceed $\pm 4\%$. The cell parameters did show a gradual change especially during the latter half of the data collection although the magnitude of the change was smaller than with the previous polymorph so the initial values were used throughout the analysis. The intensities were corrected for the gradual fluctuations of the standards and for Lorentz-polarization effects but no correction was applied for absorption. Of the 3524 independent reflections measured, 175 were considered unobserved according to $|F| \leq 6\sigma(F)$, where $|F|$ is the structure amplitude and $\sigma(F)$ is given by $[1/(2Lp|F|)] \sigma(I)$; Lp is the Lorentz-polarization factor, $\sigma(I) = [I_t + k_1^2 B + (k_2 I_t)^2]^{1/2}$, $I = I_t - B_t$, $B_t = k_1 B$, $B = (b_1 + b_2)$, $k_1 = t_s/2t_b$, $k_2 = 0.02$, $I_t = (10S + 5)$, $b_1 = (10C_1 + 5)$, $b_2 = (10C_2 + 5)$, S = the number of deacounts accumulated during the scan in time t_s , and C_1 and C_2 are

Table 1. Crystal data for thiamin pyrophosphate. $4\frac{1}{2}\text{H}_2\text{O}$

Parameters at ~ 297 K, () = e.s.d., [] = change by end of analysis; $\lambda = 1.5418$ Å.

$\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_7\text{P}_2\text{S}\cdot 4\frac{1}{2}\text{H}_2\text{O}$		
$M_r = 505.4$		Reduced cell
$a = 13.445$ (1) [+0.028] Å		$a = 6.982$ Å
$b = 12.418$ (1) [-0.010]		$b = 12.418$
$c = 6.981$ (1) [-0.017]		$c = 13.446$
$\alpha = 74.18$ (1) [-0.19]°		$\alpha = 74.41^\circ$
$\beta = 99.55$ (1) [+0.12]		$\beta = 80.45$
$\gamma = 105.59$ (1) [+0.16]		$\gamma = 74.18$
$V = 1074$ Å ³ , $Z = 2$		Space group: $P\bar{1}$ ($P1$)

$\rho_o = 1.567$ Mg m⁻³ by flotation in CCl_4 - CHCl_3

$\rho_c = 1.561$

$\mu(\text{Cu K}\alpha) = 3.36$ mm⁻¹

$F(000) = 529$

m.p. = 505 K; begins to lose water of hydration ~ 368 K. (Thermolyne melting point apparatus - uncalibrated.)

the background decacounts accumulated in time t_b at either end of the scan range.

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) with 23 of the 26 atoms correctly identified from an *E* map based on 310 reflections. The remaining non-hydrogen atoms and the oxygen atoms of four water molecules were located from a subsequent difference Fourier synthesis. The half-occupancy O(*W*5) and all of the hydrogen atoms, except some of those associated with water molecules, were located from difference Fourier syntheses after partial refinement. The structure was refined by least squares with the *CRYLSQ* program of the *XRAY* system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) which minimizes $\sum w(\Delta F)^2$. In the final stages the non-hydrogen atoms were refined with anisotropic temperature factors, the hydrogen atoms were refined with isotropic temperature factors, the parameters were blocked into four groups and w was defined by scheme 3 in *WTLSSQ* (Stewart *et al.*, 1972), with $A = 0.0$, B

$= 0.4$ and $C = 7.0$. The refinement converged at $R = 0.049$ for the 3349 observed reflections and $R = 0.050$ for all 3524 reflections.

The final difference Fourier map was relatively clean except for the customary array of peaks and holes associated with the P and S atoms. There were also small peaks in plausible locations for the missing hydrogens on the O(*W*3) and O(*W*4) water molecules, but since they would not refine they were not accepted as the hydrogen positions. The largest peak ($1.0 \text{ e } \text{Å}^{-3}$) in the difference map was associated with the disordered water molecule O(*W*5); however, the significance of this peak could not be determined. This half-occupancy water is located too close to the center of symmetry for both positions to be occupied simultaneously.* The atomic scattering factors for S, P, O, N

* It is possible that the space group is actually *P*1 with two formula units in the unit cell but only one of the O(*W*5) molecules. The results of optical second harmonic generation (Dougherty & Kurtz, 1975) indicated that one or both polymorphs could have been non-centrosymmetric but limited sample availability rendered the results inconclusive. No attempt was made to refine the structure in the non-centrosymmetric space group.

Table 2. Positional parameters with *e.s.d.*'s in parentheses

(a) Non-hydrogen atoms; fractional coordinates $\times 10^4$				(b) Hydrogen atoms; fractional coordinates and thermal parameters $\times 10^3$				
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
S(1)	-1431 (0.6)	3247 (0.7)	4238 (1)	H(2)	-28 (3)	231 (3)	371 (5)	23 (7)
C(2)	-846 (2)	2542 (3)	3221 (4)	H(3,5'1)	-149 (3)	132 (3)	-27 (5)	31 (8)
N(3)	-1306 (2)	2406 (2)	1449 (3)	H(3,5'2)	-65 (3)	256 (3)	-111 (6)	42 (9)
C(4)	-2172 (2)	2876 (2)	815 (4)	H(1')	248 (3)	210 (4)	198 (6)	46 (10)
C(5)	-2357 (2)	3366 (2)	2200 (4)	H(6')	111 (3)	287 (3)	32 (5)	44 (9)
C(3,5')	-898 (2)	1897 (3)	122 (4)	H(2'α1)	319 (5)	66 (5)	373 (9)	87 (17)
C(5')	5 (2)	1395 (2)	1140 (4)	H(2'α2)	264 (6)	948 (7)	322 (12)	144 (24)
C(6')	974 (2)	2062 (3)	1020 (4)	H(2'α3)	254 (6)	953 (7)	499 (14)	154 (26)
N(1')	1806 (2)	1630 (2)	1902 (4)	H(4'α1)	-162 (4)	-33 (4)	200 (7)	50 (11)
C(2')	1670 (2)	504 (3)	2869 (4)	H(4'α2)	-103 (3)	-116 (4)	294 (7)	42 (12)
C(2'α)	2615 (3)	89 (4)	3816 (6)	H(4α1)	-235 (4)	340 (5)	-217 (9)	83 (16)
N(3')	755 (2)	-210 (2)	3003 (4)	H(4α2)	-293 (5)	209 (6)	-146 (10)	83 (20)
C(4')	-105 (2)	205 (2)	2195 (4)	H(4α3)	-343 (4)	304 (4)	-135 (8)	67 (14)
N(4'α)	-1007 (2)	-535 (2)	2414 (4)	H(5α1)	-367 (3)	352 (4)	307 (7)	53 (11)
C(4α)	-2752 (3)	2839 (3)	-1196 (5)	H(5α2)	-355 (3)	408 (4)	61 (7)	54 (11)
C(5α)	-3211 (2)	3956 (3)	2064 (5)	H(5β1)	-230 (3)	558 (4)	155 (6)	47 (10)
C(5β)	-2820 (3)	5162 (3)	2364 (5)	H(5β2)	-337 (4)	560 (4)	222 (7)	60 (12)
O(5γ)	-2344 (2)	5076 (2)	4399 (3)	H(2-1)	-452 (5)	453 (5)	642 (9)	92 (17)
P(1)	-1893 (0.5)	6195 (0.6)	5251 (1)	H(<i>W</i> 11)	449 (4)	260 (5)	854 (9)	61 (15)
O(1-1)	-2913 (2)	6691 (2)	5036 (3)	H(<i>W</i> 12)*	419 (8)	264 (8)	1012 (15)	34 (25)
O(1-2)	-1527 (2)	5799 (2)	7381 (4)	H(<i>W</i> 21)	346 (4)	82 (5)	901 (8)	75 (15)
O(1-3)	-1189 (2)	7096 (2)	3882 (4)	H(<i>W</i> 22)	344 (5)	-18 (5)	860 (9)	82 (17)
P(2)	-3921 (0.5)	6319 (0.6)	6212 (1)	H(<i>W</i> 31)	479 (5)	881 (6)	875 (10)	97 (19)
O(2-1)	-4092 (2)	5004 (2)	7200 (3)	H(<i>W</i> 32)				
O(2-2)	-3686 (2)	6958 (2)	7825 (3)	H(<i>W</i> 41)	477 (4)	815 (5)	441 (8)	69 (16)
O(2-3)	-4792 (2)	6563 (2)	4627 (3)	H(<i>W</i> 42)				
O(<i>W</i> 1)	4361 (2)	2235 (2)	9460 (4)	H(<i>W</i> 51)				
O(<i>W</i> 2)	3028 (2)	139 (3)	8992 (4)	H(<i>W</i> 52)*	15 (9)	510 (10)	1115 (16)	23 (40)
O(<i>W</i> 3)	4466 (2)	9234 (2)	7823 (4)					
O(<i>W</i> 4)	4456 (2)	8576 (2)	4317 (4)					
O(<i>W</i> 5)*	33 (6)	4553 (6)	9012 (12)					

* Occupancy set at 0.5.

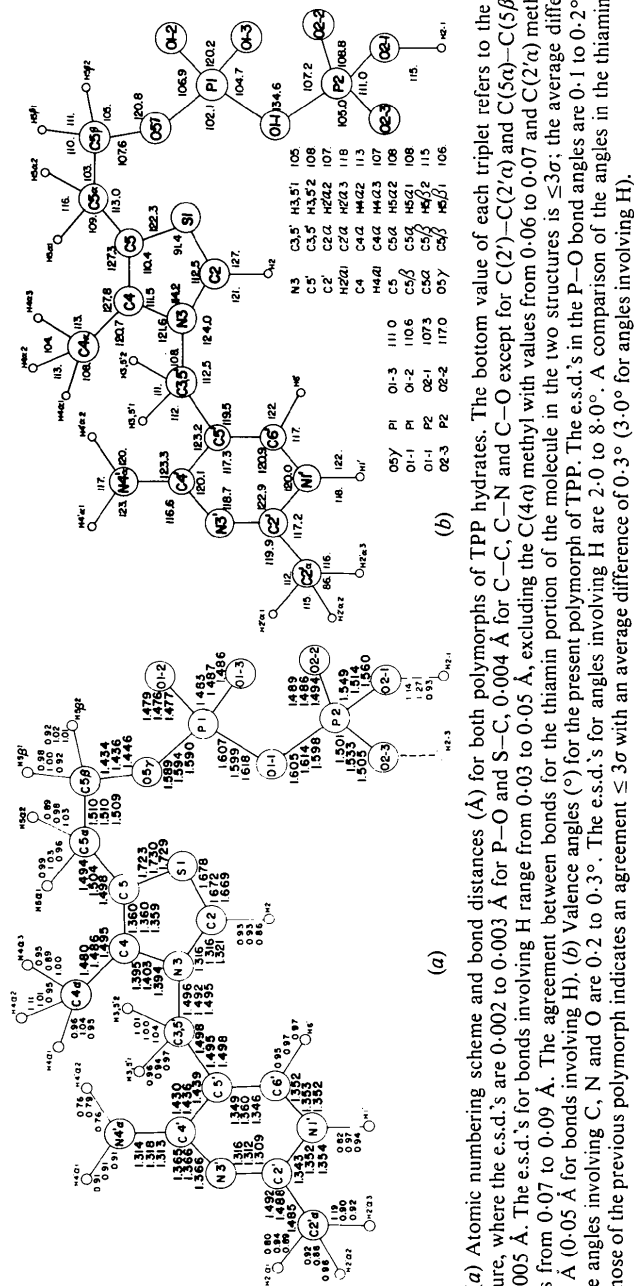


Fig. 1. (a) Atomic numbering scheme and bond distances (Å) for both polymorphs of TPP hydrates. The bottom value of each triplet refers to the present structure, where the e.s.d.'s are 0.002 to 0.003 Å for P—O and S—C, 0.004 Å for C—C, C—N and C—O except for C(2')—C(2'') and C(5 α)—C(5 β) which are 0.005 Å. The e.s.d.'s for bonds involving H range from 0.03 to 0.05 Å, excluding the C(4 α) methyl with values from 0.06 to 0.07 and C(2' α) methyl with values from 0.07 to 0.09 Å. The agreement between bonds for the thiamin portion of the molecule in the two structures is $\leq 3\sigma$; the average difference is 0.004 Å (0.05 Å for bonds involving H). (b) Valence angles ($^\circ$) for the present polymorph of TPP. The e.s.d.'s in the P—O bond angles are 0.1 to 0.2 $^\circ$. Those for the angles involving C, N and O are 0.2 to 0.3 $^\circ$. The e.s.d.'s for angles involving H are 2.0 to 8.0 $^\circ$. A comparison of the angles in the thiamin moiety with those of the previous polymorph indicates an agreement $\leq 3\sigma$ with an average difference of 0.3 $^\circ$ (3.0 $^\circ$ for angles involving H).

and C are from Cromer & Mann (1968) while that for H is from Stewart, Davidson & Simpson (1965). The anomalous-dispersion corrections for S and P are from *International Tables for X-ray Crystallography* (1968). The final positional parameters are listed in Table 2.*

Description of molecular and crystal structures

The molecular structure of this compound is very similar to those of the previous polymorph (Pletcher, Wood, Blank, Shin & Sax, 1977). This similarity is apparent from a comparison of the bond distances (Fig. 1), a comparison of the conformation of the pyrophosphate ester side chain (Fig. 2), and from the conformation with respect to the methylene bridge carbon, which is defined in terms of the torsion angles φ_T and φ_P (Pletcher, Sax, Blank & Wood, 1977). φ_T , the angle about C(3,5')—N(3), is 8.6 $^\circ$ which compares favorably with the values of 5.4 $^\circ$ and 20.5 $^\circ$ for the independent *A* and *B* molecules in the tetrahydrate polymorph. φ_P , the angle about the C(3,5')—C(5') bond, is 92.4 $^\circ$ compared with the values of 85.8 $^\circ$ and 100.5 $^\circ$ for *A* and *B* respectively. These values for the torsion angles establish the conformation as the *F* form which is the predominant conformation of thiamine when it is unsubstituted at C(2) (Shin, Pletcher, Blank & Sax, 1977).

Some of the largest differences in bond lengths between the two polymorphs are associated with the phosphate groups. These variations appear to result from differences in the phosphate oxygen bonding since the predicted values obtained by Baur's (1974) method agree well with the observed ones (Table 3). It is significant that the largest Δl is for O(1–3) which accepts a second weak hydrogen bond from C(2)—H but was not included in the calculated value. If this interaction is included, the predicted value agrees much better with the observed one.

The stacking of the planar pyridinium rings is similar to that in the other polymorph. The least-squares-planes data† show that the separation between the rings is nearly identical to those of the previous polymorph and that the extent of ring overlap here is in between the previous ones with the amino substituent of one ring lying over an adjacent ring in a manner typical of pyrimidine stacking (Bugg, Thomas, Sundaralingam &

* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34237 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The table of least-squares planes and atom displacements has been deposited. The displacements of atoms with respect to both ring systems are expressed in terms of the perpendicular distance from the ring and the projected distance in the plane to the centroid of the ring.

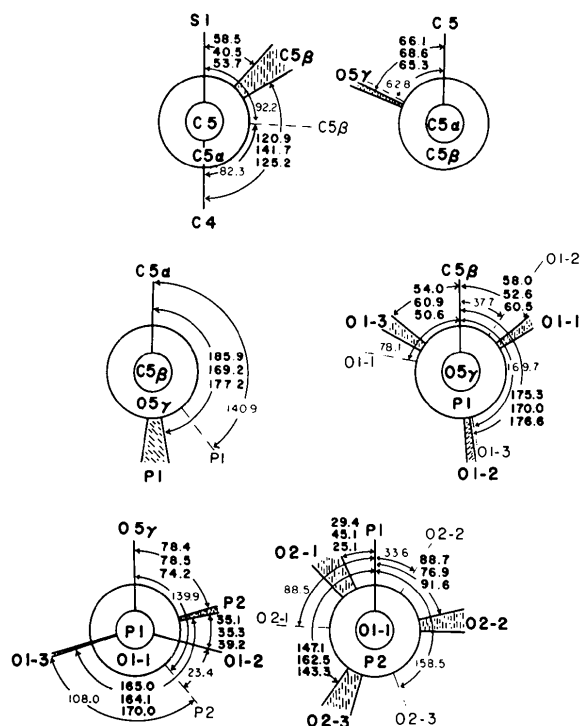


Fig. 2. Comparison of torsion angles ($^{\circ}$) in the C(5) pyrophosphate ester side chain of the four known cocarboxylase structures. The three molecules in the form of the neutral zwitterion are similar and exhibit an extended conformation. They are represented in the Newman projections in bold type with the top two values referring to molecules *A* and *B* of the previous structure and the bottom value referring to the current structure. The values for the hydrochloride structure, which has a folded conformation, are shown in light type with broken lines to designate the location of the projected atoms. The extended and folded conformations are distinguished primarily by the torsion angles about O(5 γ)-P(1) and P(1)-O(1-1).

Rao, 1971). The major difference in ring stacking between the two polymorphs is found in the crystal packing. In this structure the stacked rings form a column extending through the crystal whereas they occur in pairs in the previous one; the ring stacking is readily apparent in the stereo packing drawing of this polymorph (Fig. 3).

The hydrogen-bonding network (Table 4) involving the TPP molecule is identical with those for both *A* and *B*. However, the hydrogen bonding of the water molecules, although similar, exhibits several differences. The major consequence of these differences is the formation of a continuous spiral of hydrogen-bonded water molecules that extends through the crystal parallel to the *c* axis. In the first polymorph, the water molecules existed in clusters that were linked together only through bonds to the pyrophosphate. The additional water molecule in the present polymorph is not associated with any of the other water molecules in the unit cell.

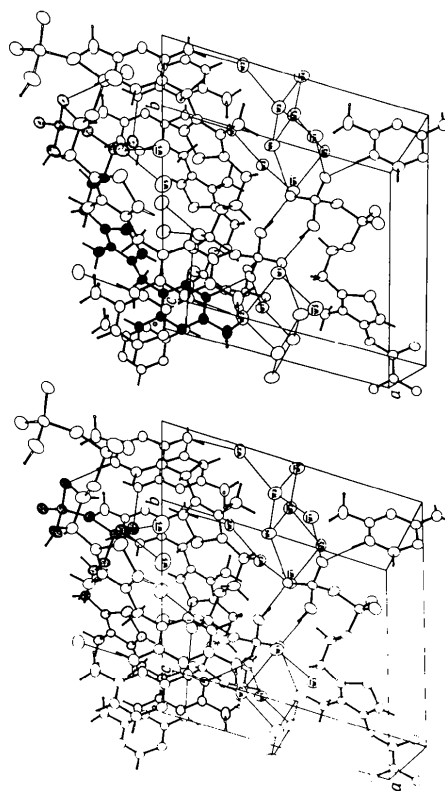


Fig. 3. Stereoscopic packing diagram of the crystal structure. The shaded atoms designate the thiamin pyrophosphate molecule whose coordinates are listed in Table 2. The water molecules, from which all hydrogen atoms have been omitted for improved clarity, are not shaded but are labeled. The ones with primed labels are related to those in Table 2 by translation only; the ones with the barred labels are centrosymmetrically related to those in the table. Hydrogen bonds are represented by a single line between atoms.

Table 3. Comparison of observed phosphate distances (\AA) and angles ($^{\circ}$) with predicted values

'Coordination' summarizes the number and types of atoms bonded to individual O atoms; H specifies a bonded hydrogen and AH designates a hydrogen-bond acceptor. 'Predicted' values are those obtained by the method of Baur (1974). The observed minus the predicted distance $\times 10^3$ is listed under $\Delta 1$. The observed minus the predicted bond angles are listed under $\Delta 2$. The $\Delta 2c$ column contains the angle differences after the predicted values have been corrected for the effect of non-bonded interactions (Wood, Sax & Pletcher, 1975; Yoo, Abola, Wood, Sax & Pletcher, 1975).

Coordination		Pre-dicted	$\Delta 1$	Pre-dicted			$\Delta 2$	$\Delta 2c$
P(1) distances				P(1) angles				
O(5 γ)	P,C	1.583	7	O(5 γ),O(1-1)	100.7	1.4	-1.4	
O(1-1)	2P	1.616	2	O(5 γ),O(1-2)	110.4	-3.5	0.6	
O(1-2)	P,AH	1.475	2	O(5 γ),O(1-3)	110.4	0.6	-0.8	
O(1-3)	P,AH	1.475	11	O(1-1),O(1-2)	108.0	2.6	1.2	
Mean Δ			6	O(1-1),O(1-3)	108.0	-3.3	0.8	
Av. P-O		1.537	6	O(1-2),O(1-3)	119.8	0.4	0.4	
				Mean $\Delta 1$		2.0	0.9	
P(2) distances				P(2) angles				
O(1-1)	2P	1.606	-8	O(1-1),O(2-1)	103.4	3.9	2.5	
O(2-1)	P,H	1.552	8	O(1-1),O(2-2)	108.0	-0.9	-0.9	
O(2-2)	P,2AH	1.487	7	O(1-1),O(2-3)	105.0	-1.4	2.7	
O(2-3)	P,3AH	1.509	-4	O(2-1),O(2-2)	112.1	-3.3	-3.3	
Mean $\Delta 1$			7	O(2-1),O(2-3)	110.4	0.6	0.6	
Av. P-O		1.539	0	O(2-2),O(2-3)	115.8	1.2	1.2	
				Mean $\Delta 1$		1.9	1.9	

Discussion

Because of the marked similarity in the crystals and molecular structure of this polymorph in comparison with the previous one, there are no new or additional

Table 4. Selected intermolecular and intramolecular contacts

(a) Hydrogen bonds				A-C (Å)	B-C (Å)	ABC (°)	
A	B	C					
N(4' α)	H(4' α 2)	...O(1-3 ⁱ)		2.795 (4)	2.05 (5)	170 (5)	
N(4' α)	H(4' α 1)	...O(W2 ⁱⁱ)		2.856 (4)	1.96 (5)	171 (4)	
N(1 ^v)	H(1 ^v)	...O(2-2 ⁱⁱⁱ)		2.672 (3)	1.73 (4)	176 (4)	
O(2-1)	H(2-1)	...O(2-3 ^{iv})		2.610 (3)	1.70 (7)	168 (6)	
O(W1)	H(W11)	...O(2-3 ⁱⁱⁱ)		2.910 (4)	2.22 (6)	168 (6)	
O(W1)	H(W12)	...O(2-2 ^v)		2.741 (4)	1.91 (10)	161 (10)	
O(W2)	H(W21)	...O(W1)		2.803 (4)	1.92 (6)	171 (6)	
O(W2)	H(W22)	...O(W3 ⁱ)		2.804 (4)	1.93 (6)	174 (6)	
O(W3)	H(W31)	...O(W1 ^v)		2.842 (4)	2.00 (7)	170 (7)	
O(W3)	H(W32)*	...O(W4)		2.780 (4)	—	—	
O(W4)	H(W41)	...O(2-3 ^{vii})		2.883 (4)	2.16 (6)	162 (6)	
O(W4)	H(W42)*	...O(W3 ^{viii})		2.848 (4)	—	—	
O(W5)	H(W51)*	...O(1-2)		2.843 (8)	—	—	
O(W5)	H(W52)*	...O(1-2 ^v)		2.960 (8)	—	—	
C(2)	H(2)	...O(1-3 ⁱⁱⁱ)		3.129 (4)	2.47 (3)	134 (3)	
(b) Close contacts around S							
C(2)	S(1)	...O(5 γ)		—	2.892 (2)	156.7 (1)	
C(5)	S(1)	...O(5 γ)		—	—	74.2 (1)	
(c) Symmetry code							
None	x	y	z	(iv)	-1-x	1-y	1-z
(i)	x	-1+y	z	(v)	-x	1-y	2-z
(ii)	-x	-y	1-z	(vi)	1-x	1-y	2-z
(iii)	-x	1-y	1-z	(vii)	1+x	y	z
				(viii)	1-x	2-y	1-z

* Not located.

inferences to be drawn from the current structure. However, it does provide added support for the conclusions drawn from the earlier structure.

The greater stability of the current polymorph (with respect to melting point and radiation sensitivity) is not readily explained by the respective crystal structures. The first polymorph gave indications that water was easily lost from the crystal, yet the hydrogen bonds

involving water molecules are the same or even slightly stronger in that structure. Also, in that structure, the water molecules form isolated clusters and do not form the continuous water column found in the current one.

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The Crystal Structure of *syn*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propellane-11,13-dione [Forms (A) and (B)]

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Abstract

C₁₂H₁₂O₅, *M_r* = 237.30; two crystalline modifications were obtained: (A) monoclinic, *P*2₁/*c*, *a* = 17.782 (8), *b* = 8.221 (4), *c* = 16.252 (8) Å, β = 115.10 (2)°, *Z* =

8, *D_x* = 1.466 Mg m⁻³; (B) monoclinic, *P*2₁/*c*, *a* = 15.191 (8), *b* = 8.375 (4), *c* = 16.819 (8) Å, β = 94.98 (2)°, *Z* = 8, *D_x* = 1.479 Mg m⁻³. Each form contains two crystallographically independent molecules in the asymmetric unit. The configuration of

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