respectively. The corresponding H···Br contacts are 2·38, 2·28 and 2·23 Å.

I wish to thank Professor S. Abrahamsson for advice and never failing support and Mrs M. Innes for technical assistance. Grants in support of the Crystallography Group were obtained from the Swedish Medical and the Swedish Natural Science Research Councils, the Swedish Board for Technical Development and the U. S. Public Health Service (GM-11653).

References

ABRAHAMSSON, S. (1959). *Acta Cryst.* **12**, 304–309.
ABRAHAMSSON, S. & LUNDÉN, B.-M. (1972). *Acta Cryst.* B**28**, 2562–2567.
ABRAHAMSSON, S., STÄLLBERG-STENHAGEN, S. & STENHAGEN, E. (1963). *Prog. Chem. Fats Other Lipids*, **7**, 67–79.
GORDON, M., STENHAGEN, E. & VAND, V. (1953). *Acta Cryst.* **6**, 739–741.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–209. Birmingham: Kynoch Press.
JELLINEK, F. (1958). *Acta Cryst.* **11**, 626–631.
JENSEN, L. H. & MABIS, A. J. (1966). *Acta Cryst.* **21**, 770–781.
LINDGREN, J. & OLOVSSON, I. (1968). *Acta Cryst.* B**24**, 554–558.
MILLS, O. S. & ROLLETT, J. S. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, pp. 107–124. Oxford: Pergamon Press.
O'CONNELL, A. M. (1968). *Acta Cryst.* B**24**, 1399–1405.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1974). B**30**, 1760

The Crystal and Molecular Structure of Trisodium 6-Phospho-D-gluconate Dihydrate, $Na_3PO_4C_6H_{10}O_6.2H_2O$ and Comparison of Results from Filtered and Monochromatic Radiation

BY G. D. SMITH, A. FITZGERALD AND C. N. CAUGHLAN
Department of Chemistry, Montana State University, Bozeman, Montana 59715, *U.S.A.*
AND K. A. KERR AND J. P. ASHMORE
Department of Physics, University of Calgary, Calgary, Alberta, Canada

(*Received* 20 *August* 1973; *accepted* 15 *March* 1974)

The crystal and molecular structure of trisodium 6-phosphogluconate dihydrate has been determined by X-ray analysis. The crystals are monoclinic, space group $P2_1$, with $a=11{\cdot}588$ (2), $b=5{\cdot}876$ (1), $c=9{\cdot}859$ (2) Å, $\beta=97{\cdot}57$ (2)° and $Z=2$. The structure was solved from the Patterson synthesis and refined by full-matrix least-squares calculations to $R=3{\cdot}4\%$ with 1878 reflexions. Bond distances and angles in the 6-phosphogluconate ion are normal. The structure is held together by an extensive hydrogen-bond network as well as sodium-ion coordination by oxygen from several 6-phosphogluconate ions. Two complete sets of data were collected out to a $\sin\theta/\lambda$ of 0·703 $Å^{-1}$ on a Picker FACS-1 diffractometer. The first set of data was collected with zirconium-filtered molybdenum radiation while the second set was collected with molybdenum radiation and a graphite monochromator. Normal and half-normal probability plots show that there are no significant differences in either the derived parameters or the structure factors.

Introduction

The pentose phosphate cycle is a source of energy to biological systems as well as a means of providing reduced nicotinamide adenine dinucleotide phosphate. One of the important intermediates in this cycle is 6-phospho-D-gluconate which has a free energy of hydrolysis that is probably comparable to the $-3{\cdot}3$ kcal $mole^{-1}$ reported for glucose-6-phosphate (*Handbook for Biochemistry*, 1970). This study was undertaken as a part of our continuing research on the structures of organic phosphates and to provide detailed structural information about this low-energy phosphate.

In addition, we have been interested in comparison of structural results obtained from filtered and monochromatized radiation. Different errors in the two data sets along with uncertainties in the polarization correction for the monochromatized radiation make such a comparison valuable.

Experimental

A clear, colorless crystal of trisodium phosphogluconate dihydrate, recrystallized from a mixture of water and ethanol, was mounted along the *b* axis. Preliminary Weissenberg photographs indicated a monoclinic space group; during the subsequent data collection the sys-

tematic absence $0k0$, $k=2n+1$ was observed, which uniquely determined the space group as $P2_1$. Lattice parameters shown in Table 1 were determined by a least-squares refinement of 26 independent 2θ values using filtered radiation. Lattice parameters derived from 2θ values obtained with monochromatic radiation agreed well with those from the filtered data; the largest difference was observed in the length of the c axis and was 0·008 Å. The crystal used for the collection of intensities was approximately $0{\cdot}1\times0{\cdot}2\times0{\cdot}4$ mm with the long dimension being coincident with the b axis.

Table 1. *Crystal data*

$Na_3PO_4C_6H_{10}O_6.2H_2O$

$a=11{\cdot}588$ (2) Å	
$b=5{\cdot}876$ (1)	$\beta=97{\cdot}57$ (2)°
$c=9{\cdot}859$ (2)	
Space group $P2_1$	$Z=2$
$\varrho_c=1{\cdot}89$ g cm^{-3}	$\varrho_o=1{\cdot}86$ g cm^{-3}
μ(Mo $K\alpha$) $=3{\cdot}83$ cm^{-1}	

Two complete sets of data were collected on an FACS-1 Picker diffractometer out to a $\sin\theta/\lambda$ of 0·703 Å^{-1}. This corresponds to a somewhat greater amount of data than is available in the copper sphere. In the first case the data were collected with zirconium-filtered Mo $K\alpha$ radiation while the second set was collected with molybdenum radiation and a graphite monochromator with a 1° mosaic spread. In both cases each reflection was scanned over a range of $1{\cdot}6°+\Delta$ by the θ–2θ scan technique where Δ is the calculated separation of the $K\alpha$ doublet. Backgrounds were counted for 40 s on either side of the peak. Three standard reflections were monitored throughout the course of each data collection. These reflections were constant to approximately one standard deviation for filtered radiation while variations of about three standard deviations were noted for monochromatized radiation. The data collected with zirconium-filtered radiation were reduced in the customary fashion. The data collected with the monochromator were reduced by the Lorentz and polarization factor given by Azaroff (1955). In both cases intensities were considered unobserved according to the criterion $I<2\sigma(I)$ and were given a weight of zero. Weights used in both refinements were calculated according to the method of Stout & Jensen (1968).* Form factors were taken from *International Tables for X-ray Crystallography* (1962). Neither absorption nor extinction corrections were applied; however both real and imaginary terms were used for the form factors of phosphorus and sodium.

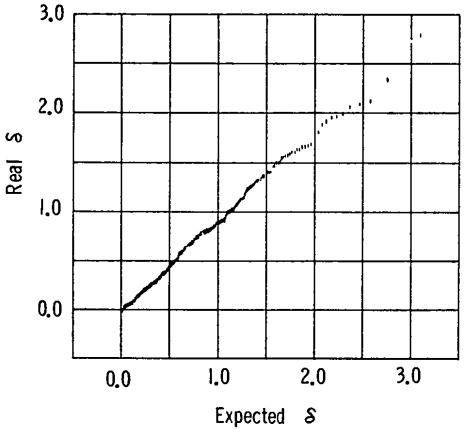

Fig. 1. Half-normal probability plot constructed from both sets of thermal and positional parameters.

Structure determination and refinement

The structure was solved by locating the phosphorus atom from a Patterson synthesis.† Several series of Fourier synthesis revealed the rest of the structure. Positional and isotropic temperature factors were refined by full-matrix least-squares calculations, minimizing the function $\sum\omega\Delta F^2$, to an R value of 5·2%. [The data set used for the initial refinement consisted of 1472 reflections; a reflection was considered observed if $I>6\sigma(I)$.] Further refinement, treating the vibration of each atom anisotropically, reduced R to 4·1%, again with the abbreviated data set. At this point a difference map was calculated which revealed the position of each hydrogen atom. Refinement of all positional parameters, anisotropic temperature factors for the heavy atoms and isotropic temperature factors for hydrogen atoms reduced R to 3·4% for the complete data set. The refinement was considered complete when the largest shift over error was less than 0·1. A difference map calculated at this point was essentially featureless, the highest positive peak being 0·3 e Å^{-3} while the most negative peak was $-0{\cdot}2$ e Å^{-3}. Positional parameters reported here are consistent with the established absolute configuration of D-gluconic acid (Pigman & Goepp, 1948).

These coordinates were then used to refine the data collected with monochromatic radiation by full-matrix least-squares calculations to an R value of 3·3%. Again, the refinement was considered complete when the largest shift over error was less than 0·1.

A $\delta(R)$ normal probability plot (Abrahams & Keve, 1971) was calculated for both sets of data; these plots were essentially linear and passed through the origin. The equation of the least-squares straight line for the filtered data was found to have a slope of 1·02 and an

* $\sigma(F)=k/4$ Lp $I[\sigma^2(I)+(0{\cdot}05I)^2]$; $\omega(F)=1/\sigma^2(F)$.

† Computer programs used were by F. R. Ahmed and coworkers (*NRC-2, Data Reduction and Tape Generation*; *NRC-8, Fourier for Distorted and Undistorted Nets*; and *NRC-12, Scan of Interatomic Distances and Angles*, National Research Council, Ottawa, Ontario, Canada; W. R. Busing and H. A. Levy (*ORFLS*) and C. K. Johnson (*ORTEP*), Oak Ridge National Laboratory, Oak Ridge, Tennessee. These programs were locally modified for use with the XDS Sigma 7 Computer. Other programs were written locally by G. D. Smith, E. L. Enwall and C. N. Caughlan.

intercept of 0·10; the slope and intercept for the monochromatized data were 1·09 and 0·12 respectively.

A half-normal probability plot (Abrahams & Keve, 1971) was constructed from the positional and thermal parameters and is illustrated in Fig. 1. The least-squares straight line through these points has a slope of 0·88 indicating that the standard deviations are slightly overestimated. A normal probability plot, constructed from the observed structure factors of both data sets is illustrated in Fig. 2. The majority of these points form an acceptably linear plot with a least-squares slope of 0·76 and an intercept of −0·1. It should also be noted that both $\delta(R)$ plots as well as the normal probability plot have a slope of approximately 0·72 in the vicinity of the origin (± 1·5 in expected δ). Thus one may conclude that the use of the monochromator does not produce a significant change in either the derived parameters or the structure factors with respect to their standard deviations.

An attempt was made to plot the ratio of the normalized structure factors from the two data sets as a function of θ. However, this produced a somewhat erratic array of points with deviations from unity of about half that noted by Hope (1971); the agreement index ($R=2\sum|F_m-F_c|/\sum|F_m+F_c|$) between the two sets of data was calculated to be 0·031. The absolute value of the deviation of the ratio F_m/F_c from unity plotted as a function of the average value of F indicated very poor agreement for the lower F values. Therefore, it would appear that a random error has been introduced due to poor counting statistics of the low intensity data and may explain the erratic behavior of the plot of the ratio of the normalized structure factors as a function of θ.

Table 2 gives the results of the two refinements. Table 3 gives the final positional and thermal parameters along with their standard deviations.*

Bond distances for the phosphogluconate ion derived from the data collected with filtered radiation are illustrated in Fig. 3. Table 4 lists the bond distances derived from the data obtained using monochromatic radiation while Table 5 lists the various bond angles for this ion.

Table 2. *Results of the refinement of the filtered and monochromatized data*

	Filtered	Monochromatized
R_{obs} ($\sum\|F_o-F_c\|/\sum\|F_o\|$)	0·034	0·033
R_ω ($[\sum\omega\Delta F^2]^{1/2}/[\sum\omega F_o^2]^{1/2}$)	0·040	0·044
R (all reflections)	0·045	0·041
S ($[\sum\omega\Delta F^2/m-n]^{1/2}$)	1·103	1·216
Number of observed reflections	1878	1930
Total number of reflections	2118	2114

* The structure factor tables for both sets of data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30416 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion of the structure

Bond distances and angles are normal with the exception of the O–H distances in the hydroxy groups. One might consider that the one P–O bond distance of 1·613 Å is much too long; however, P–O bond distances of this magnitude are not uncommon in phosphate esters. In adenosine-5′-phosphate (Kraut & Jensen, 1963), a distance of 1·610 Å is reported; 1·59 Å in glucose-1-phosphate (Beevers & Maconochie, 1965);

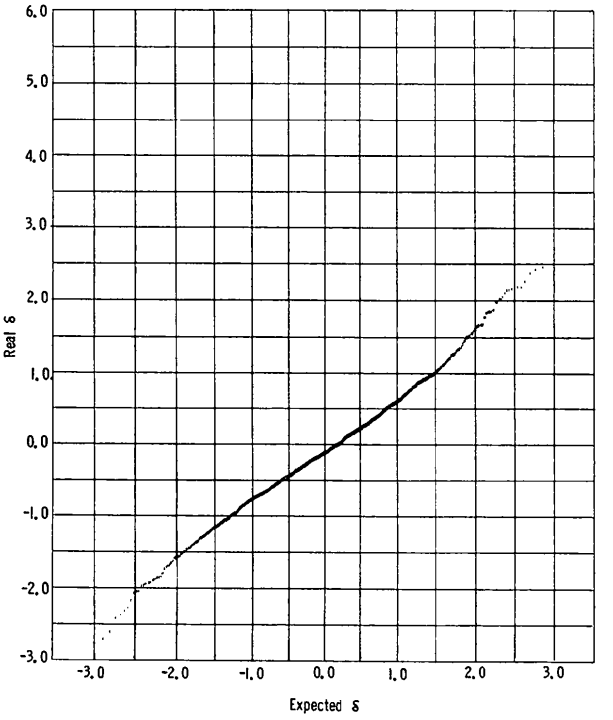

Fig. 2. Normal probability plot constructed from both sets of observed structure factors.

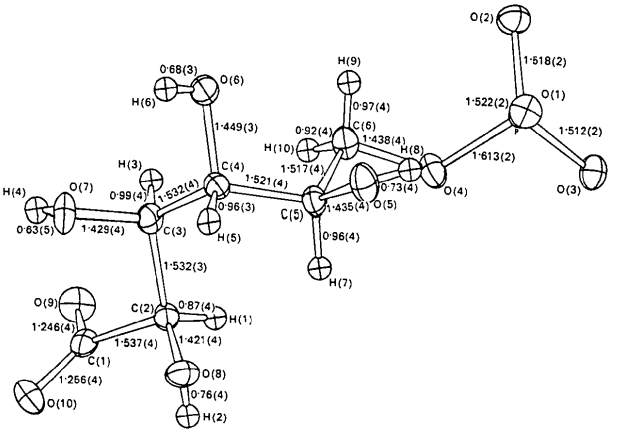

Fig. 3. *ORTEP* drawing of the phosphogluconate ion and bond distances (Å) derived from the filtered data. Thermal ellipsoids have been scaled to include 50% probability; hydrogen atoms have been assigned an isotropic temperature factor of 1·0 for the sake of clarity.

1·62 Å in β-glycerolphosphate (Haque & Caughlan, 1966) 1·612 in adenosine-3′-phosphate (Sundaralingam, 1966); and 1·616 in uridine-3′-phosphate (Viswamitra, Reddy, James & Williams, 1972). Bond angles about the phosphorus atom are considerably distorted from those of an ideal tetrahedron, but these distortions are not uncommon (Baur, 1973).

Torsion angles, calculated according to the convention of Klyne & Prelog (1960), are listed for the phosphogluconate ion in Table 6.

Hydrogen bonding

The hydrogen-bonding scheme in this structure is far from simple. There is one intramolecular hydrogen bond as well as seven other hydrogen bonds involving six different asymmetric units; these distances are listed in Table 7.

The intermolecular hydrogen bonding can be for convenience divided into three categories. The first of these involves a hydrogen bond from O(3) of one gluconate ion to H(4) of another gluconate ion which is related to the first by only a translation along the *a* axis. Thus, the net effect is to produce a one-dimensional chain of hydrogen-bonded gluconate ions which is parallel to the *a* axis of the unit cell. For the sake of clarity this is not illustrated in Fig. 4.

The second of these categories again involves one hydrogen bond from O(5) of one ion to H(2) of another ion; these pairs of hydrogen-bonded gluconate ions

Table 3. *Positional and thermal parameters with standard deviations in parentheses*

There are two entries for each atom; the first of these is the parameters derived from the filtered data while the second is those from the monochromatized data. The form of the anisotropic temperature expression is

$\exp[-(\sum_{i=1}^{3}\sum_{j=1}^{3}\beta_{ij}h_ih_j)]$. All heavy-atom parameters are $\times 10^4$ except those for P, which are $\times 10^5$.

	x/a	*y/b*	*z/c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	19281 (6)	0	9342 (6)	219 (4)	805 (17)	281 (5)	13 (9)	39 (4)	−12 (10)
	19285 (6)	0	9342 (6)	227 (4)	754 (17)	285 (5)	2 (9)	31 (4)	−12 (10)
Na(1)	463 (1)	5146 (3)	1142 (1)	43 (1)	135 (4)	70 (1)	11 (1)	11 (1)	−8 (1)
	462 (1)	5147 (3)	1140 (1)	44 (1)	127 (4)	69 (1)	12 (2)	10 (1)	−7 (2)
Na(2)	4640 (1)	8414 (2)	1133 (1)	36 (1)	114 (3)	55 (1)	−10 (2)	−4 (1)	4 (2)
	4638 (1)	8412 (2)	1133 (1)	38 (1)	107 (3)	56 (1)	−12 (2)	−5 (1)	3 (2)
Na(3)	2835 (1)	5054 (3)	9349 (1)	33 (1)	107 (3)	47 (1)	−3 (2)	6 (1)	−14 (2)
	2833 (1)	5057 (3)	9349 (1)	35 (1)	101 (3)	47 (1)	−3 (2)	7 (1)	−11 (2)
O(1)	1885 (2)	2586 (4)	856 (2)	38 (2)	79 (5)	49 (2)	8 (2)	6 (1)	7 (2)
	1885 (2)	2579 (4)	856 (2)	36 (2)	84 (6)	44 (2)	8 (2)	7 (1)	5 (3)
O(2)	721 (2)	−1038 (4)	853 (2)	25 (1)	154 (7)	53 (2)	−17 (2)	3 (1)	−8 (3)
	721 (2)	−1029 (4)	851 (2)	26 (1)	147 (7)	54 (2)	−16 (3)	5 (1)	−6 (3)
O(3)	2674 (2)	−1088 (4)	−35 (2)	39 (1)	106 (6)	38 (2)	8 (3)	11 (1)	−9 (3)
	2671 (2)	−1090 (4)	−34 (2)	39 (1)	93 (6)	36 (2)	8 (2)	12 (1)	−3 (3)
O(4)	2640 (2)	−710 (4)	2390 (2)	39 (1)	138 (6)	31 (2)	24 (2)	−3 (1)	−7 (3)
	2640 (2)	−708 (4)	2391 (2)	39 (1)	121 (6)	28 (2)	25 (2)	−2 (1)	−1 (3)
O(5)	2786 (2)	3974 (4)	3457 (2)	52 (2)	115 (6)	34 (2)	−14 (2)	1 (1)	12 (3)
	2782 (2)	3972 (4)	3454 (2)	51 (2)	124 (7)	33 (2)	−13 (3)	1 (1)	13 (3)
O(6)	1578 (2)	2966 (4)	5699 (2)	31 (1)	157 (7)	39 (2)	18 (3)	4 (1)	−8 (3)
	1578 (2)	2971 (4)	5701 (2)	32 (1)	137 (7)	39 (2)	19 (3)	3 (1)	−7 (3)
O(7)	3138 (2)	1797 (4)	8075 (2)	49 (2)	95 (6)	25 (2)	11 (3)	13 (1)	3 (3)
	3138 (2)	1789 (4)	8073 (2)	50 (2)	95 (6)	28 (2)	13 (3)	16 (1)	−3 (3)
O(8)	5194 (2)	1731 (4)	6618 (2)	26 (1)	124 (6)	52 (2)	−6 (3)	6 (1)	14 (3)
	5197 (2)	1724 (4)	6618 (2)	30 (1)	125 (6)	51 (2)	−2 (2)	6 (1)	18 (3)
O(9)	4288 (2)	−3430 (4)	8071 (2)	42 (2)	91 (6)	67 (2)	3 (2)	7 (1)	15 (3)
	4283 (2)	−3434 (4)	8070 (2)	39 (1)	87 (6)	68 (2)	4 (3)	6 (1)	21 (3)
O(10)	5476 (2)	−699 (4)	8990 (2)	39 (1)	159 (7)	39 (2)	3 (3)	−10 (1)	1 (3)
	5473 (2)	−694 (5)	8985 (2)	39 (1)	160 (7)	38 (2)	8 (3)	−8 (1)	5 (3)
O(11)	1017 (2)	5528 (4)	7809 (2)	39 (1)	168 (8)	68 (2)	4 (3)	14 (1)	−5 (3)
	1018 (2)	5535 (4)	7807 (2)	37 (1)	160 (8)	65 (2)	8 (3)	14 (1)	−2 (3)
O(12)	21 (2)	−342 (5)	6614 (2)	54 (2)	214 (10)	72 (2)	−23 (3)	1 (1)	23 (3)
	18 (2)	−337 (5)	6613 (2)	59 (2)	204 (10)	66 (2)	−26 (4)	0 (2)	15 (4)
C(1)	4780 (2)	−1549 (5)	8041 (3)	26 (2)	109 (7)	35 (2)	18 (3)	7 (1)	10 (4)
	4779 (2)	−1557 (5)	8039 (3)	27 (2)	96 (7)	37 (2)	19 (3)	9 (2)	10 (4)
C(2)	4441 (2)	−148 (5)	6733 (2)	24 (1)	87 (7)	29 (2)	8 (3)	3 (1)	2 (3)
	4439 (2)	−151 (5)	6730 (2)	23 (1)	91 (7)	29 (2)	−2 (3)	3 (1)	−8 (4)
C(3)	3205 (2)	743 (5)	6781 (3)	25 (2)	89 (7)	28 (2)	1 (3)	3 (2)	4 (3)
	3206 (2)	748 (5)	6780 (3)	27 (2)	90 (7)	27 (2)	3 (3)	3 (1)	−2 (3)
C(4)	2812 (2)	2559 (5)	5704 (3)	23 (2)	98 (7)	31 (2)	0 (3)	1 (2)	2 (3)
	2809 (2)	2562 (5)	5706 (3)	24 (2)	99 (7)	30 (2)	2 (3)	0 (2)	8 (3)
C(5)	3011 (2)	1941 (5)	4255 (3)	32 (2)	102 (7)	28 (2)	7 (4)	4 (2)	4 (4)
	3002 (2)	1943 (5)	4252 (3)	30 (2)	113 (8)	27 (2)	6 (3)	1 (2)	3 (3)
C(6)	2264 (2)	−33 (6)	3663 (3)	40 (2)	122 (7)	34 (2)	−2 (4)	5 (2)	3 (4)
	2266 (2)	−35 (6)	3663 (3)	39 (2)	112 (7)	31 (2)	−7 (4)	4 (2)	3 (4)

Table 3 (*cont.*)

Hydrogen atom parameters. Coordinates are $\times 10^3$.

	x	*y*	*z*	*B*
H(1)	442 (3)	−102 (8)	602 (3)	2·4 (8)
	438 (3)	−100 (7)	598 (3)	0·8 (6)
H(2)	580 (3)	123 (6)	666 (3)	1·2 (6)
	583 (3)	111 (7)	670 (4)	1·8 (7)
H(3)	271 (3)	−63 (6)	667 (3)	1·0 (6)
	268 (3)	−60 (6)	670 (3)	1·0 (6)
H(4)	299 (4)	106 (10)	848 (5)	5·3 (13)
	284 (5)	110 (11)	854 (6)	6·3 (15)
H(5)	324 (2)	394 (5)	589 (2)	−0·1 (5)
	325 (2)	406 (6)	591 (3)	0·3 (5)
H(6)	151 (2)	352 (6)	629 (3)	0·8 (6)
	150 (3)	350 (9)	629 (4)	2·8 (9)
H(7)	381 (3)	147 (7)	432 (3)	1·9 (7)
	385 (3)	163 (7)	435 (3)	1·6 (7)
H(8)	262 (3)	365 (9)	274 (4)	3·5 (10)
	259 (3)	364 (8)	272 (4)	2·0 (8)
H(9)	144 (3)	30 (6)	348 (3)	1·1 (6)
	141 (3)	31 (6)	354 (3)	0·6 (6)
H(10)	234 (3)	−126 (7)	424 (3)	1·2 (6)
	237 (3)	−117 (8)	426 (3)	1·8 (7)
H(11)	51 (3)	501 (7)	824 (3)	1·5 (6)
	56 (3)	513 (8)	823 (4)	2·3 (8)
H(12)	88 (3)	660 (7)	739 (4)	2·2 (8)
	81 (3)	651 (8)	738 (4)	2·2 (8)
H(13)	−49 (4)	−40 (10)	595 (4)	4·6 (12)
	−46 (4)	−49 (10)	589 (4)	4·1 (11)
H(14)	35 (4)	67 (9)	624 (4)	4·7 (12)
	42 (4)	55 (9)	621 (4)	3·7 (11)

Table 4. *Bond distances* (Å) *derived from the monochromatized data with standard deviations in parentheses*

P——O(1)	1·518 (2)	C(3)—H(3)	1·00 (4)
P——O(2)	1·517 (2)	C(3)—C(2)	1·530 (3)
P——O(3)	1·509 (2)	O(7)—H(4)	0·73 (6)
P——O(4)	1·614 (2)	C(2)—O(8)	1·422 (4)
O(4)–C(6)	1·435 (4)	C(2)—H(1)	0·89 (3)
C(6)–C(5)	1·512 (4)	C(2)—C(1)	1·539 (4)
C(6)–H(9)	1·00 (4)	O(8)—H(2)	0·81 (4)
C(6)–H(10)	0·89 (4)	C(1)—O(9)	1·246 (4)
C(5)–O(5)	1·433 (4)	C(1)—O(10)	1·255 (4)
C(5)–H(7)	0·99 (4)	O(11)–H(11)	0·76 (4)
C(5)–C(4)	1·524 (4)		0·83 (3)*
O(5)–H(8)	0·75 (4)	O(11)–H(12)	0·73 (4)
C(4)–O(6)	1·446 (3)		0·76 (4)*
C(4)–H(5)	1·02 (3)	O(12)–H(13)	0·85 (4)
C(4)–C(3)	1·530 (4)		0·82 (4)*
O(6)–H(6)	0·68 (4)	O(12)–H(14)	0·83 (5)
C(3)–O(7)	1·425 (4)		0·82 (5)*

* These distances are derived from the filtered data.

are related to each other by a twofold screw axis in the center of the cell. Here the result is a helical hydrogen-bonding scheme which extends along a line parallel to the *b* axis. This hydrogen-bonding scheme is illustrated in Fig. 4.

The third category of intermolecular hydrogen bonding involves two phosphogluconate ions as well as four water molecules. Again, hydrogen bonds are related by a twofold screw axis lying in the *bc* face of the unit cell; this is illustrated in Fig. 4. In this case, O(6) is hydrogen bonded to a water molecule through H(14).

Table 5. *Bond angles* (°) *with standard deviations in parentheses for both sets of data*

O(1)–P——O(2)	112·0 (1)*	C(5)—C(4)—C(3)	114·6 (2)
	111·8 (1)†		114·6 (2)
O(1)–P——O(3)	114·1 (1)	C(5)—C(4)—O(6)	107·9 (2)
	114·2 (1)		107·7 (2)
O(1)–P——O(4)	108·2 (1)	C(5)—C(4)–H(5)	104·1 (15)
	108·2 (1)		105·0 (17)
O(2)–P——O(3)	113·3 (1)	C(3)—C(4)–O(6)	108·7 (2)
	113·3 (1)		109·0 (2)
O(2)–P——O(4)	107·6 (1)	C(3)—C(4)—H(5)	111·0 (15)
	107·8 (1)		111·5 (17)
O(3)–P——O(4)	100·7 (1)	O(6)—C(4)—H(5)	110·3 (15)
	100·8 (1)		108·9 (17)
P——O(4)–C(6)	121·8 (2)	C(4)—O(6)—H(6)	107·5 (25)
	121·9 (2)		108·5 (37)
O(4)–C(6)–C(5)	108·9 (2)	C(4)—C(3)—C(2)	114·2 (2)
	109·1 (2)		114·5 (2)
O(4)–C(6)–H(9)	107·3 (20)	C(4)—C(3)—O(7)	105·7 (2)
	110·9 (19)		105·8 (2)
O(4)–C(6)–H(10)	108·0 (22)	C(4)—C(3)—H(3)	112·2 (19)
	110·0 (24)		112·0 (19)
C(5)–C(6)–H(9)	114·6 (20)	C(2)—C(3)—O(7)	109·7 (2)
	112·9 (19)		109·8 (2)
C(5)–C(6)–H(10)	111·1 (22)	C(2)—C(3)—H(3)	104·4 (19)
	107·6 (24)		106·7 (19)
H(9)–C(6)–H(10)	106·7 (30)	O(3)—C(3)—H(3)	110·7 (19)
	106·1 (31)		107·9 (19)
C(6)–C(5)–C(4)	113·2 (2)	C(3)—O(7)—H(4)	108·7 (47)
	113·6 (2)		114·3 (47)
C(6)–C(5)–O(5)	111·8 (2)	C(3)—C(2)—C(1)	107·1 (2)
	112·2 (2)		107·2 (2)
C(6)–C(5)–H(7)	107·6 (21)	C(3)—C(2)—O(8)	108·9 (2)
	113·4 (21)		108·9 (2)
C(4)–C(5)–O(5)	106·1 (2)	C(3)—C(2)—H(1)	107·5 (25)
	106·3 (2)		104·5 (23)
C(4)–C(5)–H(7)	105·7 (21)	C(1)—C(2)—O(8)	113·0 (2)
	102·6 (21)		112·8 (2)
O(5)–C(5)–H(7)	112·4 (21)	C(1)—C(2)—H(1)	109·9 (25)
	108·1 (21)		112·3 (23)
C(5)–O(5)–H(8)	108·6 (34)	O(8)—C(2)—H(1)	110·2 (25)
	108·7 (31)		110·6 (23)
C(2)–O(8)–H(2)	105·6 (25)	H(11)–O(11)–H(12)	118·3 (38)
	102·0 (27)		111·2 (44)
C(2)–C(1)–O(9)	115·3 (2)	H(13)–O(12)–H(14)	90·0 (47)
	115·3 (2)		90·6 (46)
O(9)–C(1)–O(10)	125·9 (3)		
	126·3 (3)		

* Upper number is that angle derived from filtered data.
† Lower number is that angle derived from monochromatized data.

Table 6. *Torsion angles* (°) *for the phosphogluconate ion*

PO(4)C(6)C(5)	−102·4
O(4)C(6)C(5)C(4)	−171·2
O(4)C(6)C(5)O(5)	65·0
C(6)C(5)C(4)C(3)	66·9
C(6)C(5)C(4)O(6)	−54·3
C(5)C(4)C(3)C(2)	49·4
C(5)C(4)C(3)O(7)	170·0
C(4)C(3)C(2)C(1)	168·5
C(4)C(3)C(2)O(8)	45·94
C(3)C(2)C(1)O(9)	72·7
C(3)C(2)C(1)O(10)	−104·6

Table 7. *Hydrogen-bond distances* (Å) *derived from the filtered data with standard deviations in parentheses*

O(1)–H(8)	2·04 (4)	O(6)—H(14)	2·08 (5)
O(2)–H(11^{i})	1·88 (3)	O(6)—H(13^{iv})	2·15 (4)
O(3)–H(4^{ii})	2·00 (5)	O(11)–H(6)	2·05 (3)
O(5)–H(2^{iii})	2·12 (4)	O(12)–H(12^{v})	2·15 (4)

The oxygen of the water molecule, O(12), is in turn bound to a symmetry-related O(6) through H(13). This helical arrangement of hydrogen bonds is the backbone of another set of hydrogen bonds through the other water molecule [O(11), H(11), H(12)] to both a phosphate oxygen and the hydrogen associated with O(6).

Table 8. *Coordination around the sodium ion derived from the filtered data*

Na(1)—O(1)	2·276 (3) Å	Na(3)—O(7)	2·341 (3) Å
Na(1)—O(2^{i})	2·285 (3)	Na(3)—O(11)	2·445 (2)
Na(1)—O(12^{ii})	2·370 (2)	Na(3)—O(3^{vii})	2·361 (3)
Na(1)—O(2^{iii})	2·350 (2)	Na(3)—O(9^{i})	2·403 (3)
O(1)—Na(1)—O(2^{i})	121·6 (1)°	Na(3)—O(1^{viii})	2·440 (3)
O(1)—Na(1)—O(12^{ii})	107·4 (1)	Na(3)—O(10^{xi})	2·421 (2)
O(1)—Na(1)—O(2^{iii})	93·0 (1)	O(7)—Na(3)—O(11)	86·4 (1)°
O(2^{i})—Na(1)—O(12^{ii})	106·6 (1)	O(7)—Na(3)—O(3^{vii})	161·0 (1)
O(2^{i})—Na(1)—O(2^{iii})	104·9 (1)	O(7)—Na(3)—O(9^{i})	81·8 (1)
O(12^{ii})–Na(1)—O(2^{iii})	124·2 (1)	O(7)—Na(3)—O(1^{viii})	87·3 (1)
Na(2)—O(3^{i})	2·431 (2) Å	O(7)—Na(3)—O(10^{xi})	92·8 (1)
Na(2)—O(10^{vi})	2·493 (2)	O(11)—Na(3)—O(3^{vii})	87·7 (1)
Na(2)—O(8^{v})	2·412 (2)	O(11)—Na(3)—O(9^{i})	103·8 (1)
Na(2)—O(9^{vi})	2·311 (3)	O(11)—Na(3)—O(1^{viii})	91·4 (1)
Na(2)—O(10^{v})	2·423 (3)	O(11)—Na(3)—O(10^{xi})	173·9 (1)
O(3^{i})—Na(2)—O(10^{vi})	73·4 (1)°	O(3^{vii}) –Na(3)—O(9^{i})	82·2 (1)
O(3^{i})—Na(2)—O(8^{v})	116·2 (1)	O(3^{vii})–Na(3)—O(1^{viii})	110·9 (1)
O(3^{i})—Na(2)—O(9^{vi})	119·5 (1)	O(3^{vii})–Na(3)—O(10^{xi})	94·9 (1)
O(3^{i})—Na(2)—O(10^{v})	93·1 (1)	O(9^{i})—Na(3)—O(1^{viii})	160·6 (1)
O(10^{vi})–Na(2)—O(8^{v})	150·7 (1)	O(9^{i})—Na(3)—O(10^{xi})	82·1 (1)
O(10^{vi})–Na(2)—O(9^{vi})	82·4 (1)	O(1^{viii})–Na(3)—O(10^{xi})	82·5 (1)
O(10^{vi})–Na(2)—O(10^{v})	101·0 (1)		
O(8^{v})—Na(2)—O(9^{vi})	92·4 (1)		
O(8^{v})—Na(2)—O(10^{v})	68·5 (1)		
O(9^{vi})—Na(2)—O(10^{v})	147·3 (1)		

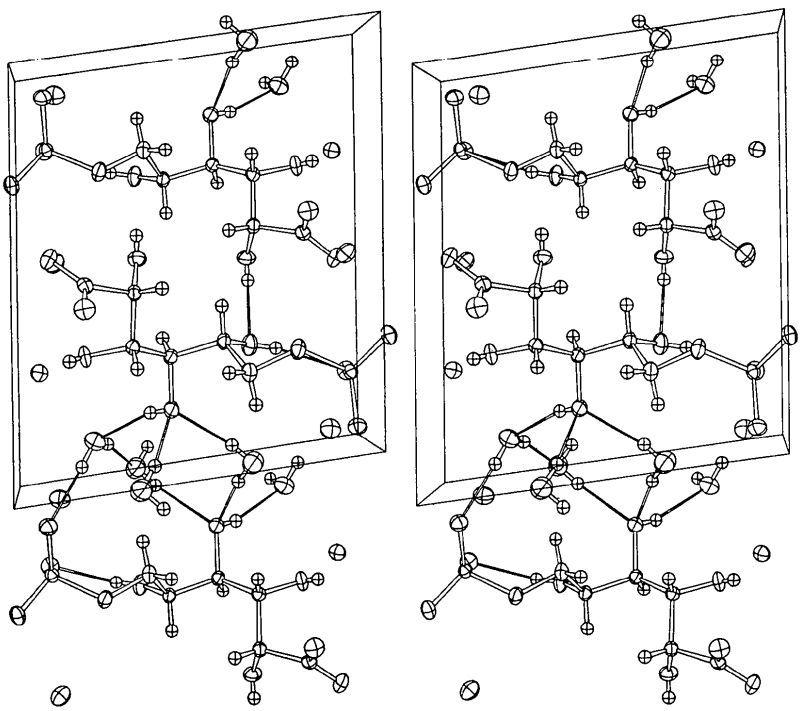

Fig. 4. *ORTEP* drawing illustrating both the packing in the unit cell as well as hydrogen bonding. The drawing is oriented with the *a* axis horizontal, the *c* axis vertical and *b* axis into the plane of the paper. Thermal ellipsoids have been scaled to include 50% probability; hydrogen atoms have been assigned an isotropic temperature factor of 1·0. The bond radius for hydrogen bonds is less than half that of covalent bonds.

The total effect of this arrangement is to produce a three-dimensional network of hydrogen bonds throughout the crystal. With the exception of O(4), O(9) and O(10), every oxygen is the acceptor of a hydrogen bond; every hydrogen associated with an oxygen atom is also involved in a hydrogen bond.

Sodium coordination

The coordination around sodium is unusual in that each sodium ion exhibits a different coordination number. Distances between sodium ion and oxygen range from 2·276(3) to 2·493(2) Å. The coordination of Na(1) may best be described as a distorted tetrahedron; Na(2) coordination is a distorted tetragonal pyramid; while Na(3) coordination is that of a distorted octahedron. Bond distances and angles between sodium and its nearest neighbors are summarized in Table 8. Two slightly longer distances of 2·816(2) and 2·759(3) Å are observed between Na(2) and oxygen; the next closest distance between sodium ion and oxygen is 3·183 (2) Å.

We wish acknowledge the National Science Foundation for a grant (GP-33598X) for partial support of this research. We also wish to thank the Montana State University Computing Center for a grant of computing time.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.
AZAROFF, L. V. (1955). *Acta Cryst.* **8**, 701–704.
BAUR, W. H. (1973). Amer. Cryst. Assoc., Abs. Papers (Winter Meeting), 144
BEEVERS, C. A. & MACONOCHIE, G. H. (1965). *Acta Cryst.* **18**, 232–236.
Handbook for Biochemistry (1970). p. J185. Cleveland, Ohio: Chemical Rubber Co.
HAQUE, M. U. & CAUGHLAN, C. N. (1966). *J. Amer. Chem. Soc.* **88**, 4123–4128.
HOPE, H. (1971). *Acta Cryst.* A**27**, 392–393.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 203, 215. Birmingham: Kynoch Press.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521.
KRAUT, J. & JENSEN, L. H. (1963). *Acta Cryst.* **16**, 79–88.
PIGMAN, W. W. & GOEPP, R. M. (1948). *Chemistry of the Carbohydrates*, p. 30. New York: Academic Press.
STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. New York: Macmillan.
SUNDARALINGAM, J. (1966). *Acta Cryst.* **21**, 495–506.
VISWAMITRA, M. A., REDDY, B. S., JAMES, M. N. G. & WILLIAMS, G. J. B. (1972). *Acta Cryst.* B**28**, 1108–1116.

Acta Cryst. (1974). B**30**, 1766

The Crystal Structure of a Flavin Molecular Complex: 10-Propylisoalloxazine–Bis(naphthalene-2,3-diol)

BY MING C. KUO, JOHN B. R. DUNN AND CHARLES J. FRITCHIE JR

Richardson Chemical Laboratories, Tulane University, New Orleans, La. 70118, *U.S.A.*

(*Received* 18 *December* 1973; *accepted* 12 *March* 1974)

The crystal structure of the orange molecular complex 10-propylisoalloxazine–bis(naphthalene-2,3-diol), a possible model for enzymic flavin–substrate interactions, has monoclinic symmetry and space group $A2/a$. There are eight formula groups, $C_{13}H_{12}N_4O_2.2C_{10}H_8O_2$, in the unit cell having constants $a=26{\cdot}69$ (3), $b=7{\cdot}246$ (8), $c=29{\cdot}20$ (4) Å, and $\beta=102{\cdot}51$ (3)°. The calculated density is 1·39 g cm^{-3}; the measured value is 1·40 g cm^{-3}. The final R index, based on 869 statistically observed, counter-measured reflections, is 4·0%. Half the naphthalene-2,3-diol molecules alternate with the isoalloxazines in a ···DADA··· type stack running parallel to **b**; the remainder lie between stacks and are hydrogen bonded to N(1) and O(2) of the flavins. Intermolecular spacings within the stacks are 3·38 and 3·46 Å, the shorter involving a naphthalenediol interaction with the pyrimidinoid and pyrazinoid rings of the flavin and the longer with the phenylene and pyrazinoid rings. Flavins are base-paired by N(3)H(3)···O(2) hydrogen bonds across C_2 axes, and O(4) of each flavin is also hydrogen bonded to a hydroxyl group of a stacked naphthalenediol molecule. Both naphthalenediol molecules exhibit internal OH···O hydrogen bonding.

Introduction

Isoalloxazine or flavin (I) is an essential component of electron-transfer processes in many biological systems. It is found in nature as a prosthetic group in the form of riboflavin 5′-phosphate, FMN, or the pyrophosphate, FAD, produced by linking FMN with adenosine 5′-phosphate. When the flavin prosthetic