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## Zwitterionic Character of Guanosine 5'-Monophosphate (5'-GMP): Redetermination of the Structure of 5'-GMP Trihydrate

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**Abstract.**  $C_{10}H_{14}N_5O_8P \cdot 3H_2O$ ,  $M_r = 417$ ,  $P2_12_12_1$ ,  $a = 10.649$  (2),  $b = 6.185$  (1),  $c = 25.514$  (4) Å,  $Z = 4$ ,  $V = 1680.3$  Å<sup>3</sup>,  $D_o = 1.644$  (floatation in 2-propanol/CHBr<sub>3</sub>),  $D_c = 1.648$  Mg m<sup>-3</sup>,  $\mu = 2.14$  mm<sup>-1</sup> (Cu K $\alpha$ ). A redetermination of the structure of 5'-GMP·3H<sub>2</sub>O [originally reported by Murayama, Nagashima & Shimizu (1969). *Acta Cryst.* **B25**, 2236–2245] has established that the nucleotide exists as a zwitterion with the N(7) site of the base protonated. The three water molecules of hydration bridge the base N(7) and a phosphate oxygen of the same molecule through hydrogen bonding. One of the H atoms on the base N(2) atom appears to be involved in a bifurcated hydrogen bond, while an anionic phosphate O atom simultaneously accepts hydrogen bonds from the base N(1) and N(2) atoms. There is also a hydrogen bond to the ribose ring O(4') atom.

**Introduction.** Recently, Sundaralingam & Prusiner (1978) predicted zwitterionic character for the free acid

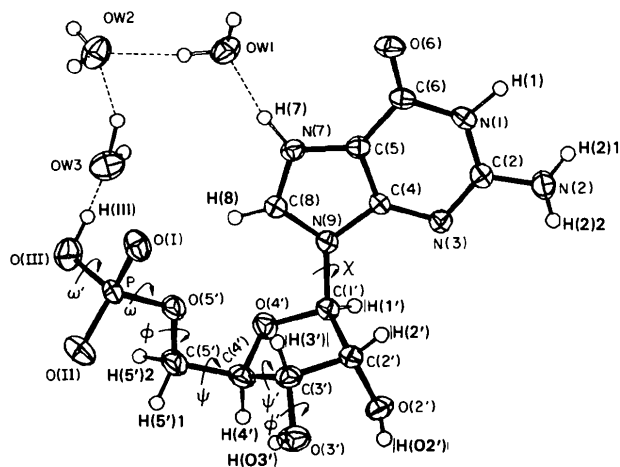


Fig. 1. An ORTEP drawing of 5'-GMP·3H<sub>2</sub>O showing the molecular conformation, atom numbering and conformational notations.

of guanosine 5'-monophosphate (5'-GMP). In the published crystal structure of 5'-GMP.3H<sub>2</sub>O (Murayama, Nagashima & Shimizu, 1969) only some of the H atoms were located and zwitterionic character for the nucleotide was not suspected. We have carried out a careful redetermination of the crystal structure of 5'-GMP.3H<sub>2</sub>O, located all the H atoms and established that the nucleotide exists as a zwitterion. The N(7) site of the imidazole moiety is protonated and the phosphate negatively charged (Fig. 1).

The free acid of guanosine 5'-monophosphate was purchased from Sigma Chemical Company (St Louis, Missouri) and crystallized by slow evaporation from aqueous solution. A crystal (1.0 × 0.45 × 0.20 mm) was mounted for data collection with its *b* axis coincident with the  $\phi$  axis of a Picker FACS-1 diffractometer. The accurate cell constants were determined and the intensities of 1618 reflections (1612 > 1.5 $\sigma$ ) were collected in the manner described in our previous paper (Emerson & Sundaralingam, 1980). The crystal parameters are given in the *Abstract*. The unit-cell dimensions obtained by Murayama *et al.* (1969) are: *a* = 10.64, *b* = 6.18, *c* = 25.58 Å.

The structure was determined by the Patterson heavy-atom method, as was done by the earlier workers. The refinement of all 24 heavy atoms of the nucleotide and the three water O atoms was performed by full-matrix least-squares methods. After several cycles of isotropic and anisotropic refinement of the heavy atoms, the positions of all 20 H atoms, including that attached to the N(7) atom of the base, were located in difference Fourier maps. The positional coordinates and isotropic temperature factors of the 20 H atoms were also refined. At the conclusion of the refinement, the *R* index was 0.030 and the secondary-extinction parameter *g* (equation 3; Larson, 1967) was 0.754 × 10<sup>-5</sup>. Residual peaks of about 0.20 e Å<sup>-3</sup> were located between some of the P—O bonds. The maximum shift/ $\sigma$  ratios in the atomic parameters were 0.08 for the heavy atoms and 0.3 for the H atoms. The weighting scheme used was based on counting statistics, where weight = 1/[ $\sigma_F^2 + (0.007 \times |F_{obs}|)^2$ ].

**Discussion.** The atomic coordinates and their associated e.s.d.'s are given in Table 1.\* An *ORTEP* (Johnson, 1965) drawing of the molecule is shown in Fig. 1 and bond distances and bond angles are given in Fig. 2. Table 2 lists conformation angles of interest for the nucleotide. Average standard deviations are 0.002 Å for the bond lengths involving the P atom and 0.003 Å for those involving the other heavy atoms. The

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35055 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters for the atoms of 5'-GMP.3H<sub>2</sub>O*

*B*<sub>iso</sub> for the non-hydrogen atoms is calculated by the expression  $B_{iso} = \frac{1}{3} \sum_i \sum_j \beta_{ij} (a_i, a_j)$ . Note that the positional coordinates published by the earlier authors (Murayama *et al.*, 1969) correspond to the wrong (L) enantiomorph.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>iso</sub> (Å <sup>2</sup> )
P	0.11495 (5)	0.29725 (10)	0.52617 (2)	1.76
N(1)	0.05597 (18)	0.68233 (33)	0.83820 (7)	2.04
C(2)	0.18535 (22)	0.68452 (37)	0.83770 (8)	1.84
N(2)	0.24190 (19)	0.69293 (39)	0.88410 (7)	2.52
N(3)	0.25308 (17)	0.67982 (32)	0.79421 (7)	1.92
C(4)	0.18115 (20)	0.67357 (38)	0.75058 (7)	1.57
C(5)	0.05280 (21)	0.67370 (40)	0.74744 (8)	1.81
C(6)	-0.02122 (21)	0.67658 (35)	0.79456 (9)	1.82
O(6)	-0.13630 (15)	0.67211 (30)	0.79772 (7)	2.61
N(7)	0.02099 (17)	0.67219 (32)	0.69522 (7)	1.90
C(8)	0.12561 (21)	0.66779 (39)	0.66746 (8)	1.95
N(9)	0.22524 (16)	0.66608 (32)	0.69966 (7)	1.78
C(1')	0.35973 (21)	0.65890 (40)	0.68452 (9)	1.96
C(2')	0.41783 (20)	0.43751 (42)	0.69590 (9)	2.10
O(2')	0.54735 (15)	0.47601 (33)	0.70488 (6)	2.72
C(3')	0.39458 (20)	0.31903 (43)	0.64426 (9)	2.22
O(3')	0.48265 (16)	0.14967 (32)	0.63668 (7)	3.07
C(4')	0.40824 (21)	0.49723 (44)	0.60360 (9)	2.24
O(4')	0.36671 (15)	0.69433 (28)	0.63016 (6)	2.34
C(5')	0.33414 (23)	0.46510 (53)	0.55415 (9)	2.85
O(5')	0.20754 (15)	0.40116 (34)	0.56840 (6)	2.75
O(I)	0.01336 (17)	0.19630 (31)	0.55837 (6)	2.77
O(II)	0.18526 (18)	0.16331 (35)	0.48824 (7)	3.31
O(III)	0.06134 (18)	0.49879 (35)	0.49524 (7)	3.12
O(W1)	0.77971 (15)	0.69128 (32)	0.66621 (7)	2.93
O(W2)	0.71101 (18)	0.70413 (32)	0.56219 (7)	3.28
O(W3)	0.96682 (19)	0.76712 (31)	0.56266 (8)	3.45
H(1)	0.0161 (22)	0.6826 (44)	0.8741 (8)	2.5 (5)
H(2)1	0.1955 (25)	0.7085 (46)	0.9110 (10)	3.6 (6)
H(2)2	0.3189 (22)	0.6886 (44)	0.8830 (8)	2.6 (5)
H(7)	-0.0614 (24)	0.6791 (47)	0.6803 (10)	3.7 (6)
H(8)	0.1241 (17)	0.6662 (35)	0.6327 (7)	1.1 (4)
H(1')	0.3973 (18)	0.7804 (37)	0.7039 (8)	1.9 (5)
H(2')	0.3775 (20)	0.3773 (46)	0.7266 (9)	2.8 (5)
H(O2')	0.5855 (28)	0.3636 (68)	0.7036 (13)	7.4 (10)
H(3')	0.3065 (24)	0.2669 (50)	0.6449 (10)	3.8 (6)
H(O3')	0.4501 (34)	0.0212 (69)	0.6237 (11)	7.0 (9)
H(4')	0.4949 (19)	0.5120 (35)	0.5941 (7)	1.1 (4)
H(5')1	0.3790 (23)	0.3527 (47)	0.5325 (10)	3.4 (6)
H(5')2	0.3315 (31)	0.5927 (61)	0.5253 (11)	6.2 (8)
H(III)	0.0164 (30)	0.5813 (64)	0.5173 (11)	6.5 (9)
H(W1)1	0.7110 (32)	0.6514 (65)	0.6801 (12)	7.0 (9)
H(W1)2	0.7641 (26)	0.6821 (60)	0.6321 (9)	4.7 (7)
H(W2)1	0.6689 (28)	0.7953 (52)	0.5482 (11)	5.3 (8)
H(W2)2	0.7013 (30)	0.5938 (59)	0.5435 (11)	5.5 (8)
H(W3)1	0.8746 (25)	0.7455 (46)	0.5613 (10)	4.1 (7)
H(W3)2	0.9803 (37)	0.9003 (66)	0.5552 (13)	8.7 (11)

standard deviations in the corresponding bond angles are 0.1 and 0.3° respectively. The bond distances and bond angles of the present analysis are generally in agreement with those previously determined (Murayama *et al.*, 1969; note some typographical errors in their Fig. 2). The precision obtained in the present refinement is about three times better than in the earlier work.

Protonation of the guanine base at N(7) was established by examination of difference electron density maps. The H atom on N(7) was located in the map at a density of 0.41 e Å<sup>-3</sup>. The effect of protona-

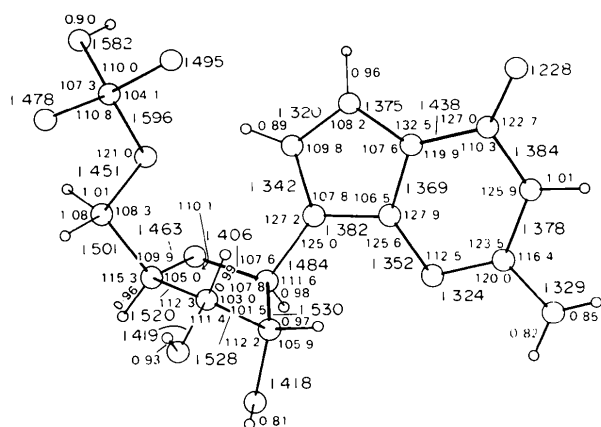


Fig. 2. Bond distances (Å) and bond angles (°) in 5'-GMP·3H<sub>2</sub>O. The e.s.d.'s are given in the text.

Table 2. Conformation angles for guanosine 5'-monophosphate trihydrate

The torsion angle notations are after Sundaralingam (1969) (see also Pullman, Saenger, Sasisekharan, Sundaralingam & Wilson, 1973). The pseudorotation parameters ( $P, \tau_m$ ) are after Altona & Sundaralingam (1972).

Glycosyl torsion angle	10.7 (3)°
Backbone torsion angles	
$\omega$	-81.1 (2)
$\phi$	-164.4 (3)
$\psi$	46.5 (3)
$\psi'$	88.2 (3)
Phase angle, $P$	4.7 (8) ( $^3T_2$ )
Amplitude of puckering, $\tau_m$	35.7 (3)
C(5')-O(5')-P-O(I)	163.7
C(5')-O(5')-P-O(II)	34.0 (2)

tion on the base geometry has already been discussed (Sundaralingam & Prusiner, 1978) and will not be detailed here.

Hydrogen-bond distances and angles are listed in Table 3 and a stereoscopic packing diagram is shown in Fig. 3. It is interesting that a string of three water molecules connect the base site N(7) and the phosphate oxygen O(III), as shown in Fig. 1. The protonated N(7) site is directly hydrogen bonded to a water O rather than to an anionic phosphate O as is usually observed in nucleotide zwitterions. One of the H atoms on the amino N atom is a donor in a hydrogen bond to a phosphate O atom. The other amino H atom, H(2)1, appears to be involved in a bifurcated hydrogen bond to an anionic phosphate O atom, O(II), and the ribosyl hydroxyl O(3') atom. The other anionic phosphate O atom, O(1), is simultaneously involved in hydrogen bonding to the base N(1) and N(2) atoms. The 2'-hydroxyl group hydrogen bonds to the ring N(3) atom while the 3'-hydroxyl group hydrogen bonds to the furanoid ring O(4') atom of a translated molecule. Involvement of the furanoid ring O atom in hydrogen bonding has been observed in several nucleoside structures, especially their analogs (Sprang, Scheller, Rohrer & Sundaralingam, 1978). The H atoms on the water molecules are hydrogen bonded to other waters and all three phosphate O atoms. The carbonyl group C(6)-O(6) is sandwiched between two imidazole rings of translated guanine bases and is shielded from hydrogen bonding.

The zwitterionic character of the monomeric nucleotide building blocks (AMP, CMP, GMP) common to both DNA and RNA (Sundaralingam & Prusiner, 1978) parallels the zwitterionic nature of the amino acid building blocks of proteins. The enhanced

Table 3. Hydrogen-bond distances and angles in guanosine 5'-monophosphate trihydrate

$$\sigma(A-H) = \sigma(H \cdots B) \approx 0.02 \text{ \AA}, \sigma(A \cdots B) \approx 0.003 \text{ \AA}, \sigma(A-H \cdots B) \approx 2-3^\circ.$$

Bond $A-H \cdots B$	Symmetry Translation		Distance (Å)	Angle (°)
	code for $B^*$	for $B$ $x y z$		
N(1)-H(1)···O(I)	4	0 0 1	1.01	165
N(2)-H(2)1···O(I)	4	0 0 1	0.85	144
N(2)-H(2)1···O(II)	2	0 1 0	0.85	113
N(2)-H(2)2···O(3')	4	1 0 1	0.82	168
N(7)-H(7)···O(W1)	1	1 0 0	0.96	168
O(2')-H(O2')···N(3)	4	1 1 1	0.81	154
O(3')-H(O3')···O(4')	1	0 1 0	0.93	155
O(III)-H(III)···O(W3)	1	1 0 0	0.90	165
O(W1)-H(W1)1···O(2')	1	0 0 0	0.85	157
O(W1)-H(W1)2···O(W2)	1	0 0 0	0.89	172
O(W2)-H(W2)1···O(III)	3	0 1 1	0.80	173
O(W2)-H(W2)2···O(II)	3	0 0 1	0.84	171
O(W3)-H(W3)1···O(W2)	1	0 0 0	0.99	164
O(W3)-H(W3)2···O(I)	1	1 1 0	0.86	164

\* Symmetry codes are: (1)  $x, y, z$ ; (2)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ ; (3)  $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$ ; (4)  $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$ .

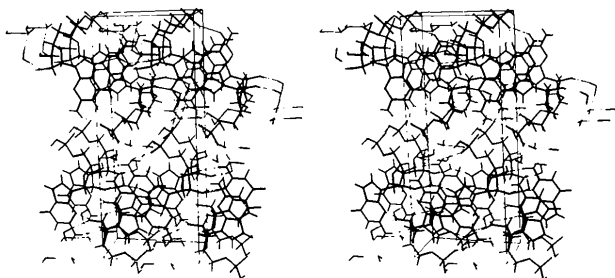


Fig. 3. A stereoscopic packing diagram for 5'-GMP · 3H<sub>2</sub>O.

solubility of the zwitterions in aqueous solution may have played an important role in the formation of the corresponding polymers under primordial conditions.

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Structure of Tetrabromo-*p*-phenylene Bis(toluene-*p*-sulphonate)

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**Abstract.** C<sub>20</sub>H<sub>14</sub>Br<sub>4</sub>O<sub>6</sub>S<sub>2</sub>, M<sub>r</sub> = 734.1, triclinic, P $\bar{1}$ , *a* = 7.555 (2), *b* = 9.396 (2), *c* = 10.470 (2) Å,  $\alpha$  = 109.71 (1),  $\beta$  = 112.98 (2),  $\gamma$  = 101.02 (2)°, *Z* = 1, *D*<sub>c</sub> = 2.04, *D*<sub>m</sub> = 2.00 Mg m<sup>-3</sup>, *V* = 597.9 (2) Å<sup>3</sup>. X-ray data were obtained on an automatic four-circle Syntex P2<sub>1</sub> diffractometer. The structure was refined to *R* = 0.046. The dihedral angle between the planes of the first and second benzene rings is 48.6 (5)°.

**Introduction.** This work is part of a study on the conformation of bis(toluene-*p*-sulphonate) derivatives of tetrasubstituted (by Br, Cl, CH<sub>3</sub>) hydroquinones. Results for tetramethyl- and tetrachloro-*p*-phenylene bis(toluene-*p*-sulphonate) (Wieczorek, Boki & Struchkov, 1975; Wieczorek & Gałdecki, 1978) have proved that toluene-*p*-sulphonate groups are in a *trans* orientation. Single crystals of tetrabromo-*p*-phenylene bis(toluene-*p*-sulphonate) were grown from chloroform/cyclohexane solutions. Intensity data were collected on a Syntex P2<sub>1</sub> four-circle diffractometer. Measurements were carried out in the  $\theta$ - $2\theta$  scan mode

for  $3.5 \leq 2\theta \leq 50^\circ$  and an absorption correction was applied [ $\mu(\text{Mo } K\alpha) = 6.78 \text{ mm}^{-1}$ ]. With the application of the acceptance criterion  $F \geq 4.0\sigma(F)$ , 1399 unique reflections were retained for the refinement. The structure was solved by direct methods with *SHELX* 76 (Sheldrick, 1976) and refined by blocked-full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. The methyl H atoms were refined as part of rigid methyl groups. The remaining H atoms were subjected to the constraint  $d(\text{C-H}) = 1.08 \pm 0.02$  Å, with individual isotropic temperature factors. The terminal value of *R*<sub>w</sub> was 0.038 with *R* 0.046.\* Weights were given by  $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ , where *k* and *g* were refined to 1.7559 and 0.0003 respectively. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman,

\* Lists of structure factors, thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35060 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.