

Tableau 3. *Plans moyens*

Plan moyen 1 défini par N(1), C(3), C(4), C(5), C(6), C(7), C(8), C(9)
Equation du plan $0,873x - 0,457y + 0,167z = 3,367$

| Atomes | N(2) | N(1) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) |
|------------------------|-------|-------|-------|--------|-------|-------|--------|--------|--------|
| Distances au plan en Å | 0,066 | 0,029 | 0,011 | -0,015 | 0,031 | 0,012 | -0,025 | -0,017 | -0,027 |

Plan moyen 2 défini par N(1), N(2), C(3)
Equation du plan $0,844x - 0,454y + 0,110z = 3,138$

Plan moyen 3 défini par les atomes C(4), C(5), C(6), C(7), C(8), C(9)
Equation du plan $0,869x - 0,458y + 0,185z = 3,392$

Angle dièdre du plan N° 2 avec le plan N° 3: 4,4°

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The Crystal Structure of Disodium Deoxyguanosine-5'-phosphate Tetrahydrate

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The crystal structure of disodium deoxyguanosine monophosphate tetrahydrate has been determined from data collected on a Siemens four-circle diffractometer. The crystals are monoclinic, space group $P2_1$, with $a = 5.556$, $b = 10.763$, $c = 15.774$ Å, $\beta = 97^\circ 55'$, $Z = 2$. The structure was solved by Patterson methods. The final R for 1196 reflexions is 0.037. The glycosidic torsion angle, defined by $O(4')-C(1')-N(9)-C(4)$, is 236.9° . The sugar ring pucker relative to the least-squares plane through the five-atom sugar ring is $O(4')$ -endo, $C(4')$ -exo. The orientation of the $C(5')-O(5')$ bond is *gauche* relative to the $C(4')-O(4')$ bond and *trans* relative to the $C(4')-C(3')$ bond. One of the Na ions has an octahedral coordination of six oxygen atoms whilst the other is five-coordinated in a distorted square-based pyramidal arrangement. Two of the phosphate oxygens are involved in Na coordination.

Introduction

The structure determination of disodium deoxyguanosine-5'-phosphate (Na_2GDRP) was undertaken as part of a series of structural studies of nucleosides and nucleotides. Structural studies of three of the four commonly occurring nucleotides found in DNA have already been made, namely thymidine-5'-phosphate (Trucblood, Horn & Luzzati, 1961), deoxycytidine-5'-phosphate (Viswamitra, Reddy, Lin & Sundaralingam, 1971) and deoxyadenosine-5'-phosphate (Reddy & Viswamitra, 1973). The structure determination of GDRP (Fig. 1)

completes the studies of the commonly occurring nucleotides in DNA. An account of the implications of the conformational parameters of GDRP has been given (Young, Tollin & Wilson, 1974).

Experimental

Crystals of disodium GDRP tetrahydrate ($\text{C}_{10}\text{H}_{12}\text{N}_5\text{O}_7\text{P} \cdot \text{Na}_2 \cdot 4\text{H}_2\text{O}$), grown by slow evaporation from aqueous solutions, and as observed in the commercial preparation, were in the form of thin plates. Weissenberg and precession photographs established that

the crystals were monoclinic, with systematic absences consistent with the space groups $P2_1$ and $P2_1/m$ and the asymmetry of the nucleotide establishes the space group as $P2_1$. The cell dimensions, obtained by least-squares analysis of measurements on the diffractometer with Mo $K\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$), are $a=5.556 (2)$, $b=10.763 (4)$, $c=15.774 (5) \text{ \AA}$, $\beta=97^\circ 55 (3)'$.

The calculated density, with one GDRP ion, two sodium ions, and four molecules of water per asymmetric unit is 1.646 g cm^{-3} .

Two sets of intensities were collected, one on a Hilger and Watts linear diffractometer, with Mo $K\alpha$ radiation and balanced filters, and the other on a Siemens four-circle diffractometer with crystal-monochromatized Mo $K\alpha$ radiation. The data were collected to an angle corresponding to the limiting sphere for Cu $K\alpha$ radiation. Two crystals were used to obtain the linear diffractometer data, one mounted along **a** and the other along **b**. Data were collected on the layer planes $h=0$ to 4 and $k=0$ to 11, and 1845 unique non-zero reflexions were measured out of a possible 2298 within the range $0^\circ \leq 2\theta \leq 56^\circ$.

The second set of data was collected with a third crystal, and 1196 non-zero reflexions were measured. R' between the two independent sets of data, for the common reflexions, was 0.04 where $R' = \sum |F_1 - kF_2| / \sum F_1$, k being the scaling factor. The crystals were very small and no absorption corrections were used. Although fewer significant data were obtained with the four-circle diffractometer, this set was considered to be more reliable because no scaling was required between layer planes, and this set was used in the structure determination and refinement.

Structure determination

A sharpened Patterson function was calculated and the largest peak in the Harker section was assumed to indicate the P-P vector. There were several other large peaks in the section and one of these was assumed to indicate one of the Na-Na vectors. An electron density map was calculated with phases obtained from these phosphorus

and sodium positions. $R = \sum ||F_{\text{calc}}| - |F_{\text{obs}}|| / \sum |F_{\text{obs}}|$ was 0.47 at this stage.

A rotation function (Tollin & Munns, to be published) was calculated from a model of a phosphate group. The largest peak in this function indicated the orientation of the phosphate group. An independent examination of the electron density projected down the short axis confirmed this orientation. The function $I(\theta\varphi)$ (Tollin & Cochran, 1964) which determines the orientation of planar groups was calculated and indicated the orientation of the purine moiety. The largest peak in the $I(\theta\varphi)$ function at $\theta=81$, $\varphi=49^\circ$ was just 2° in each coordinate away from the final refined direction of the purine plane normal.

Phases were calculated with the PO_4 group and the sodium ion, and two oxygen atoms at positions suggested by the first electron density map, one of which turned out later to be the second sodium ion. An electron density map revealed the positions of 28 of the heavy atoms and phases were calculated with these positions included. R was 0.24 and the resulting electron density map revealed the remaining heavy atoms; their inclusion reduced R to 0.20.

Refinement

The structure was refined by block-diagonal least-squares calculation. A program written by Professor J. Trotter, modified for use on an Elliott 4130 computer, was used.

Unit weights were assigned to all structure amplitudes for which $|F_{\text{obs}}| \leq 30.0$ while for all the others the weight was $30.0/|F_{\text{obs}}|$. In four cycles of least-squares refinement in which the coordinates and individual isotropic thermal parameters of the non-hydrogen atoms were refined, R fell to 0.062.

A difference synthesis gave the locations of 17 of the hydrogen atoms. The positions of those hydrogen atoms which could be calculated from geometrical considerations fitted well with some of the largest peaks in this difference map, as did some of those involved in hydrogen bonding.

Further refinement of the parameters of the non-hydrogen atoms was carried out, keeping the hydrogen atoms fixed and assigning to them isotropic temperature factors $B=3.0 \text{ \AA}^2$. The thermal parameters of the non-hydrogen atoms were anisotropic and of the form

$$\exp [-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{23}kl + B_{13}hl)]$$

and individual weights, w , given by

$$w = 1 / \{1 + (|F_o| - b)^2 / a^2\}$$

initially with $a=8.0$ and $b=12.0$, were assigned to each structure factor. After a further three cycles, when R was 0.048, a final difference synthesis revealed two of the missing hydrogen atoms. The last hydrogen, attached to $W(3)$, was not in the position expected if it were involved in the hydrogen-bonding scheme suggested by the intermolecular bond scan. The largest

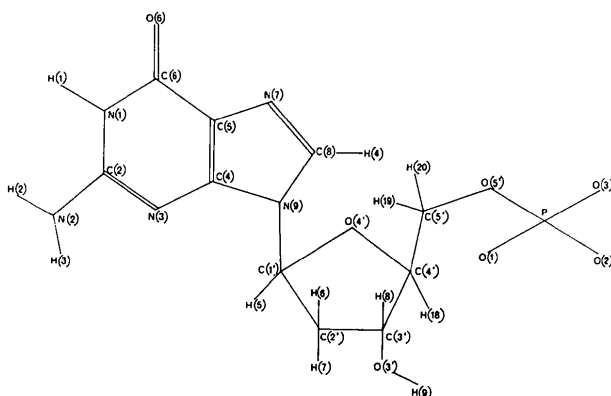


Fig. 1. The GDRP ion and the atom numbering.

peak in the region of $W(3)$ in the difference map, of height 0.31 e \AA^{-3} , was identified as the missing hydrogen since bond lengths and angles for this peak were quite acceptable. The next largest peak in this region was of height 0.26 e \AA^{-3} and the map as a whole had density fluctuations varying in height from 0.2 to -0.2 e \AA^{-3} .

A re-examination of the $\langle wA^2 \rangle$ values as a function of $|F_{\text{obs}}|$ suggested that a and b in the weighting scheme should be changed to 12.0 and 15.0 respectively. This was effected and further cycles of least-squares refinement carried out in which, in alternate cycles, the hydrogen atom parameters were allowed to vary. In the final stages the root-mean-square shifts in the positional and thermal parameters of the non-hydrogen atoms were 0.19σ and 0.41σ respectively, where σ is the estimated standard deviation.

The final R for the 1196 reflexions collected on the Siemens diffractometer, and used in the least-squares refinement, was 0.037 . Incorporation of the weak reflexions collected on the Hilger and Watts diffractometer gave an R of 0.069 for the 1845 reflexions. Finally with all the unobserved reflexions within the Cu $K\alpha$ limiting sphere set to 0.7 of the significant structure amplitude in the appropriate region of reciprocal space, R was 0.098 .†

Results and discussion

The values of the positional and thermal parameters of the heavy atoms and their estimated standard deviations are given in Tables 1 and 3. The positional parameters of the hydrogen atoms are given in Table 2. The bond lengths and angles involving the heavy atoms are given in Table 4. The average estimated standard deviations in bond lengths are $\sigma(\text{P-O})=0.004 \text{ \AA}$ and $\sigma(\text{C, N, O-C})=0.007 \text{ \AA}$, and the average estimated standard deviations in bond angles are $\sigma(\text{P-O-C})=0.3^\circ$, $\sigma(\text{C-O-C, C-C-O})=0.4^\circ$ and $\sigma(\text{C-C-C, C-N-C, N-C-C})=0.5^\circ$. In Table 5 the bond lengths and angles involving the hydrogen atoms are listed. The average estimated standard deviation in these bond lengths is 0.07 \AA , and the average estimated standard deviations in bond angles are $\sigma(\text{C-C-H, C-N-H, N-C-H})=2.5^\circ$ and $\sigma(\text{H-C-H, H-O-H})=5.6^\circ$.

The purine base

The purine base is essentially planar and the equation of the least-squares plane through the ring atoms is

$$0.6153x + 0.7645y + 0.1922z - 4.718 = 0$$

where x , y and z are coordinates, in \AA , measured relative to \mathbf{a} , \mathbf{b} and \mathbf{c}^* . The maximum deviation of a

† A copy of this final data set with the observed and calculated structure amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30440 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional parameters of the non-hydrogen atoms, with estimated standard deviations ($\times 10^4$)

| | x/a | y/b | z/c |
|-------|-----------|-----------|----------|
| N(1) | 2089 (8) | 3454 (4) | 6964 (3) |
| C(2) | 1078 (10) | 4047 (5) | 6224 (3) |
| N(2) | -733 (10) | 4832 (6) | 6288 (3) |
| N(3) | 1812 (8) | 3862 (5) | 5463 (3) |
| C(4) | 3704 (10) | 3063 (5) | 5515 (3) |
| C(5) | 4871 (10) | 2445 (5) | 6218 (3) |
| C(6) | 4043 (10) | 2630 (5) | 7034 (3) |
| O(6) | 4791 (8) | 2148 (4) | 7724 (2) |
| N(7) | 6741 (9) | 1718 (5) | 5994 (3) |
| C(8) | 6720 (11) | 1905 (6) | 5184 (4) |
| N(9) | 4901 (9) | 2720 (4) | 4846 (3) |
| C(1') | 4327 (10) | 3089 (6) | 3944 (3) |
| C(2') | 6334 (11) | 3790 (6) | 3579 (3) |
| C(3') | 6392 (10) | 3211 (5) | 2688 (3) |
| O(3') | 6106 (7) | 4087 (4) | 2014 (2) |
| C(4') | 4225 (10) | 2284 (5) | 2595 (3) |
| O(4') | 3968 (7) | 1964 (4) | 3463 (2) |
| C(5') | 4747 (11) | 1120 (5) | 2115 (3) |
| O(5') | 2730 (7) | 281 (4) | 2093 (2) |
| O(1) | -862 (7) | -888 (4) | 1461 (2) |
| O(2) | 2668 (7) | -651 (4) | 610 (2) |
| O(3) | 56 (7) | 1197 (4) | 816 (3) |
| P | 1041 (2) | -21 (2) | 1188 (1) |
| Na(1) | 7285 (4) | 347 (2) | 8446 (1) |
| Na(2) | 5723 (4) | -2124 (2) | 905 (1) |
| W(1) | 349 (8) | -1296 (4) | 9006 (2) |
| W(2) | 4331 (7) | -4040 (4) | 235 (2) |
| W(3) | 9280 (8) | 181 (5) | 7228 (3) |
| W(4) | 9620 (8) | -3301 (4) | 894 (3) |

Table 2. Positional parameters of the hydrogen atoms, with estimated standard deviations ($\times 10^3$)

| | x/a | y/b | z/c |
|-------|-----------|-----------|---------|
| H(1) | 159 (11) | 357 (6) | 748 (4) |
| H(2) | -149 (13) | 492 (8) | 674 (5) |
| H(3) | -153 (14) | 523 (8) | 584 (5) |
| H(4) | 786 (15) | 160 (7) | 485 (5) |
| H(5) | 277 (14) | 359 (8) | 397 (5) |
| H(6) | 774 (14) | 368 (8) | 393 (5) |
| H(7) | 598 (12) | 469 (6) | 354 (4) |
| H(8) | 793 (12) | 282 (6) | 270 (4) |
| H(9) | 728 (13) | 409 (8) | 174 (5) |
| H(10) | -23 (18) | -185 (10) | 907 (6) |
| H(11) | 109 (15) | -105 (9) | 945 (5) |
| H(12) | 516 (14) | -447 (7) | 5 (5) |
| H(13) | 347 (17) | -384 (9) | -11 (6) |
| H(14) | 848 (16) | 62 (9) | 695 (6) |
| H(15) | 1028 (17) | 56 (9) | 740 (6) |
| H(16) | 968 (16) | -331 (8) | 45 (5) |
| H(17) | 972 (14) | -266 (8) | 102 (5) |
| H(18) | 287 (12) | 277 (7) | 236 (4) |
| H(19) | 612 (13) | 69 (7) | 244 (5) |
| H(20) | 487 (13) | 128 (7) | 155 (4) |

ring atom from this plane is 0.015 \AA (Table 6), but the deviations of the attached atoms N(2), O(6) and C(1') from the plane are significantly larger.

The bond lengths and angles in the guanine base are in good agreement with those found in related structures (Voet & Rich, 1970).

The sugar

The pucker of the sugar ring in GDRP is rather unusual in that relative to the mean plane through the

Table 3. *Thermal parameters of the non-hydrogen atoms, with estimated standard deviations ($\times 10^5$)*

| | B_{11} | B_{22} | B_{33} | B_{12} | B_{23} | B_{13} |
|-------|------------|----------|----------|------------|-----------|-----------|
| N(1) | 1916 (149) | 376 (38) | 154 (15) | 169 (132) | -9 (42) | 398 (78) |
| C(2) | 1837 (161) | 395 (43) | 177 (17) | 323 (173) | 63 (56) | 267 (90) |
| N(2) | 2753 (175) | 737 (53) | 269 (19) | 1102 (168) | 117 (59) | 534 (94) |
| N(3) | 1852 (140) | 395 (40) | 180 (16) | 225 (138) | 35 (43) | 388 (80) |
| C(4) | 1753 (162) | 281 (40) | 142 (16) | -70 (152) | 64 (48) | 248 (86) |
| C(5) | 1592 (155) | 365 (41) | 159 (17) | 500 (153) | 21 (48) | 252 (89) |
| C(6) | 1936 (167) | 256 (39) | 121 (16) | 129 (151) | 53 (44) | 176 (87) |
| O(6) | 2359 (135) | 524 (37) | 194 (14) | 527 (130) | 53 (41) | 427 (70) |
| N(7) | 2261 (156) | 477 (42) | 193 (16) | 734 (149) | -11 (49) | 416 (82) |
| C(8) | 2264 (189) | 538 (53) | 199 (20) | 552 (188) | 54 (57) | 480 (99) |
| N(9) | 1774 (131) | 388 (41) | 147 (16) | 270 (134) | -6 (41) | 183 (80) |
| C(1') | 1801 (165) | 437 (47) | 150 (18) | 174 (166) | -22 (51) | 327 (90) |
| C(2') | 2358 (187) | 445 (48) | 186 (19) | -519 (178) | -65 (55) | 387 (102) |
| C(3') | 1718 (165) | 286 (42) | 165 (17) | -253 (150) | -50 (48) | 206 (92) |
| O(3') | 2017 (125) | 467 (35) | 231 (15) | -54 (120) | 169 (42) | 410 (71) |
| C(4') | 1320 (148) | 387 (42) | 135 (16) | -267 (149) | -65 (51) | 136 (83) |
| O(4') | 2267 (126) | 365 (31) | 139 (12) | -699 (113) | -60 (35) | 329 (65) |
| C(5') | 1771 (165) | 380 (43) | 169 (18) | -360 (160) | -139 (51) | -32 (95) |
| O(5') | 1829 (111) | 442 (32) | 141 (12) | -589 (114) | 89 (36) | 141 (61) |
| O(1) | 1787 (119) | 479 (34) | 188 (13) | -578 (117) | -17 (39) | 104 (68) |
| O(2) | 1602 (111) | 438 (32) | 163 (13) | 96 (116) | -86 (37) | 218 (65) |
| O(3) | 2280 (138) | 305 (31) | 246 (15) | 417 (121) | 83 (39) | 137 (77) |
| P | 1213 (32) | 252 (8) | 117 (3) | -105 (42) | -8 (13) | 130 (18) |
| Na(1) | 2084 (69) | 474 (20) | 229 (8) | -40 (70) | -111 (22) | 197 (39) |
| Na(2) | 1835 (66) | 426 (19) | 199 (7) | 90 (66) | -33 (21) | 224 (37) |
| W(1) | 2368 (136) | 430 (33) | 197 (14) | -229 (125) | -45 (40) | 106 (75) |
| W(2) | 1708 (124) | 574 (38) | 228 (15) | 459 (125) | -116 (43) | 229 (71) |
| W(3) | 2868 (144) | 700 (44) | 263 (15) | 931 (152) | 147 (49) | 257 (79) |
| W(4) | 2527 (146) | 478 (36) | 286 (17) | 346 (131) | -150 (44) | 313 (84) |

Table 4. *Bond lengths (Å) and angles (°) for the heavy atoms*

| | | | |
|-------------|-------|-------------------|-------|
| N(1)-C(2) | 1.381 | N(2)-C(2)-N(1) | 116.9 |
| C(2)-N(2) | 1.330 | N(2)-C(2)-N(3) | 119.4 |
| N(1)-C(6) | 1.395 | N(1)-C(2)-N(3) | 123.7 |
| C(6)-O(6) | 1.225 | C(2)-N(1)-C(6) | 125.6 |
| C(5)-C(6) | 1.437 | N(1)-C(6)-O(6) | 120.3 |
| C(4)-C(5) | 1.377 | N(1)-C(6)-C(5) | 110.9 |
| C(2)-N(3) | 1.331 | C(5)-C(6)-O(6) | 128.8 |
| N(3)-C(4) | 1.353 | C(4)-C(5)-C(6) | 118.9 |
| C(5)-N(7) | 1.386 | C(4)-C(5)-N(7) | 110.7 |
| N(7)-C(8) | 1.294 | C(6)-C(5)-N(7) | 130.4 |
| C(4)-N(9) | 1.374 | C(2)-N(2)-C(4) | 111.9 |
| C(8)-N(9) | 1.388 | N(2)-C(4)-C(5) | 129.0 |
| N(9)-C(1') | 1.468 | N(2)-C(4)-N(9) | 125.5 |
| C(1')-C(2') | 1.523 | C(5)-C(4)-N(9) | 105.4 |
| C(1')-O(4') | 1.428 | C(4)-N(9)-C(8) | 106.2 |
| C(2')-C(3') | 1.544 | C(4)-N(9)-C(1') | 127.4 |
| C(3')-C(4') | 1.552 | C(8)-N(9)-C(1') | 126.3 |
| C(3')-O(3') | 1.414 | N(7)-C(8)-N(9) | 112.7 |
| C(4')-O(4') | 1.439 | C(5)-N(7)-C(8) | 105.0 |
| C(4')-C(5') | 1.510 | N(9)-C(1')-C(2') | 115.3 |
| C(5')-O(5') | 1.436 | N(9)-C(1')-O(4') | 106.3 |
| O(5')-P | 1.629 | C(2')-C(1')-O(4') | 106.1 |
| P-O(1) | 1.516 | C(1')-O(4')-C(4') | 106.0 |
| P-O(2) | 1.529 | C(1')-C(2')-C(3') | 104.6 |
| P-O(3) | 1.508 | C(2')-C(3')-O(3') | 113.5 |
| | | C(2')-C(3')-C(4') | 103.4 |
| | | C(4')-C(3')-O(3') | 110.6 |
| | | C(3')-C(4')-O(4') | 104.1 |
| | | C(3')-C(4')-C(5') | 112.2 |
| | | O(4')-C(4')-C(5') | 109.2 |
| | | C(4')-C(5')-O(5') | 109.5 |
| | | C(5')-O(5')-P | 120.0 |
| | | O(5')-P-O(1) | 102.4 |
| | | O(5')-P-O(2) | 107.1 |
| | | O(5')-P-O(3) | 107.6 |
| | | O(1)-P-O(2) | 112.9 |
| | | O(1)-P-O(3) | 114.5 |
| | | O(2)-P-O(3) | 111.5 |

Table 5. *Bond lengths (Å) and angles (°) involving hydrogen atoms*

| | | | |
|-------------|------|-------------------|-------|
| N(1)-H(1) | 0.91 | C(2)-N(1)-H(1) | 124.4 |
| N(2)-H(2) | 0.86 | C(2)-N(2)-H(2) | 125.0 |
| N(2)-H(3) | 0.90 | C(2)-N(2)-H(3) | 122.7 |
| C(8)-H(4) | 0.93 | N(7)-C(8)-H(4) | 127.6 |
| C(1')-H(5) | 1.00 | N(9)-C(1')-H(5) | 99.0 |
| C(2')-H(6) | 0.91 | O(4')-C(1')-H(5) | 113.0 |
| C(2')-H(7) | 0.99 | C(2')-C(1')-H(5) | 116.0 |
| C(3')-H(8) | 0.97 | C(1')-C(2')-H(6) | 109.0 |
| C(4')-H(18) | 0.95 | C(1')-C(2')-H(7) | 110.4 |
| C(5')-H(19) | 0.97 | H(6)-C(2')-H(7) | 108.8 |
| C(5')-H(20) | 0.94 | C(3')-C(2')-H(6) | 113.2 |
| O(3')-H(9) | 0.84 | C(3')-C(2')-H(7) | 110.9 |
| W(1)-H(10) | 0.71 | C(2')-C(3')-H(8) | 109.0 |
| W(1)-H(11) | 0.82 | O(3')-C(3')-H(8) | 106.7 |
| W(2)-H(12) | 0.74 | C(4')-C(3')-H(8) | 113.8 |
| W(2)-H(13) | 0.74 | C(3')-O(3')-H(9) | 111.1 |
| W(3)-H(14) | 0.73 | C(5')-C(4')-H(18) | 117.1 |
| W(3)-H(15) | 0.72 | O(4')-C(4')-H(18) | 108.6 |
| W(4)-H(16) | 0.73 | C(3')-C(4')-H(18) | 104.8 |
| W(4)-H(17) | 0.74 | C(4')-C(5')-H(19) | 109.8 |
| | | C(4')-C(5')-H(20) | 112.7 |
| | | O(5')-C(5')-H(19) | 103.9 |
| | | O(5')-C(5')-H(20) | 105.2 |
| | | H(19)-C(5')-H(20) | 115.2 |
| | | H(10)-W(1)-H(11) | 111.1 |
| | | H(12)-W(2)-H(13) | 105.7 |
| | | H(14)-W(3)-H(15) | 100.4 |
| | | H(16)-W(4)-H(17) | 108.3 |

five atoms of the ring, O(4') has maximum deviation of 0.24 Å, on the same side as C(5') and N(9), and C(4') has the next largest deviation of 0.20 Å on the opposite side of the mean plane. The pucker is thus O(4')-endo, C(4')-exo. This type of pucker has previously only been observed in the nucleoside dihydrothy-

Table 6. Deviations (Å) of atoms from the least-squares plane of the purine moiety

| | |
|-------|--------|
| N(1) | 0.000 |
| C(2) | 0.015 |
| N(3) | -0.009 |
| C(4) | -0.013 |
| C(5) | -0.005 |
| C(6) | -0.001 |
| N(7) | -0.002 |
| C(8) | 0.012 |
| N(9) | 0.003 |
| N(2) | 0.056 |
| O(6) | -0.024 |
| C(1') | -0.039 |

midine (Konnert, Karle & Karle, 1970), which also has a deoxyribose sugar. Comparison of the sugar ring pucker in the four 5'-deoxynucleotides shows that there is a marked variation (Table 9), whereas for the corresponding 5'-ribose nucleotides (Sundaralingam, 1973) the puckers fall into one or other of the categories C(3')-endo, C(2')-exo or C(2')-endo, C(3')-exo.

The equation of the least-squares plane through the five ring atoms is

$$0.7141x - 0.6080y + 0.3472z - 1.3885 = 0$$

and the deviations of atoms from this plane are listed in Table 7. The torsion angles around the sugar ring are listed in Table 8 and are similar to those in dihydrothymidine.

Table 7. Deviations (Å) of atoms from the least-squares plane of the five-atom sugar ring

| | | | |
|-------|--------|-------|--------|
| C(1') | -0.163 | O(4') | 0.242 |
| C(2') | 0.033 | C(5') | 0.580 |
| C(3') | 0.090 | O(3') | -0.859 |
| C(4') | -0.201 | N(9) | 0.653 |

Table 8. The torsion angles around the sugar ring

| | |
|-------------------------|--------|
| C(2')-C(1')-O(4')-C(4') | 322.2° |
| C(1')-O(4')-C(4')-C(3') | 40.3 |
| O(4')-C(4')-C(3')-C(2') | 333.4 |
| C(4')-C(3')-C(2')-C(1') | 4.6 |
| C(3')-C(2')-C(1')-O(4') | 19.3 |

The orientation of the C(5')-O(5') bond relative to the furanose ring is *gauche* relative to the C(4')-O(4') bond and *trans* to C(4')-C(3'). This *gauche-trans* con-

formation, although found in quite a few nucleosides (Wilson, 1973; Sundaralingam, 1973) has been observed previously in only one 5'-nucleotide, 6-azauridine-5'-phosphate (Saenger & Suck, 1973).

Conformation of the GDRP molecule

The orientation of the sugar ring relative to the purine base, described in terms of rotation about the glycosidic bond for the sequence of atoms O(4')C(1')N(9)C(4) is 236.9° and the nucleotide is in the *anti* conformation (Donohue & Trueblood, 1960). The dihedral angles giving the conformation about C(4')-C(5') and C(5')-O(5') are given in Table 9 with the corresponding conformational parameters for the other 5'-deoxynucleotides.

Phosphate group

The phosphate group is in the staggered conformation relative to O(5')-C(5'), with torsion angles C(5')-O(5')-P-O(2) = 61.8°, C(5')-O(5')-P-O(1) = 180.8° and C(5')-O(5')-P-O(3) = 302.1°.

The phosphate group in GDRP is present as the divalent anion RPO_4^{2-} , as in calcium thymidylate (Trueblood, Horn & Luzzati, 1961). Two of the phosphate oxygens, O(1) and O(2), are each involved in two hydrogen bonds and O(3) is involved in three hydrogen bonds. O(1) and O(2) are also involved in the Na(2) coordination, whereas O(3) is not. If the charges on the phosphate group reside on oxygen atoms then two of the bonds should be P-O⁻ bonds and the third a P=O bond, which should be shorter. The shortest P-O bond is the P-O(3) bond, which suggests that the charges on the phosphate group reside mainly on O(1) and O(2), which are the ones involved in the Na coordination. However, it should be noted that P-O(2) is significantly longer than P-O(1), as might be expected since O(2) is closer to the Na(2) ion than O(1), and this suggests that other valence bond structures contribute to the resonance state of the phosphate group.

Sodium coordination

The coordination about the two sodium ions is shown in Fig. 2, and the relevant distances and angles are given in Table 10. There are two types of sodium coordination. For Na(1) there is octahedral coordination involving the four water molecules and O(3') of one GDRP molecule and O(6) of another. Na(2),

Table 9. A summary of the conformational parameters in GDRP and in other 5'-deoxynucleotides

χ_{CN} is defined for the sequence O(4')C(1')N(9)C(4), Ψ for C(3')C(4')C(5')O(5'), and ϕ for C(4')C(5')O(5')P.

| Compound | χ_{CN} | Sugar pucker | Ψ | ϕ | Reference |
|--|--------------------|----------------------|--------|--------|---|
| Thymidine-5'-phosphate hexahydrate, Ca salt | 223.3° | C(3')-endo-C(4')-exo | 57.2° | 204.0° | Trueblood, Horn & Luzzati (1961) |
| Deoxycytidine-5'-phosphate monohydrate | 182.1 | C(3')-exo-C(4')-endo | 57.3 | 166.0 | Viswamitra, Reddy, Lin & Sundaralingam (1971) |
| Deoxyadenosine-5'-phosphate hexahydrate, Na salt | 249.7 | C(2')-endo-C(1')-exo | 62.6 | 112.8 | Reddy & Viswamitra (1973) |
| Deoxyguanosine-5'-phosphate tetrahydrate, Na ₂ salt | 236.9 | O(4')-endo-C(4')-exo | 175.4 | 112.8 | Present work |

however, is only five-coordinated, with a distorted square-pyramidal geometry. Two of the atoms involved are phosphate oxygens O(1) and O(2), and one edge of the pyramid is common to the octahedron about

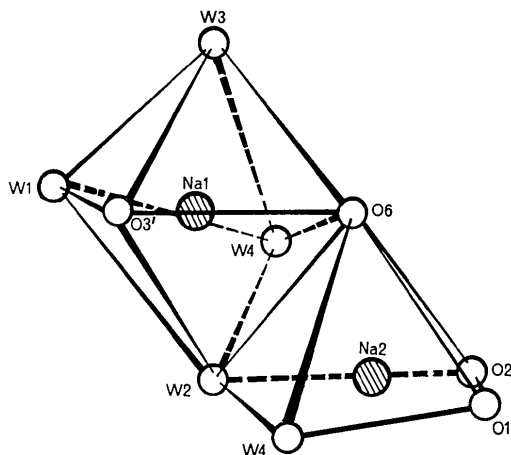


Fig. 2. The sodium ion environments.

Table 10. Sodium coordination distances and angles
The average e.s.d. for bond lengths is 0.005 Å and for bond angles 0.3°.

| | | | |
|------------------|------------------|-----------------|---------|
| Na(1)-W(1) (1+x | y | z) | 2.527 Å |
| -W(2) (1-x | $\frac{1}{2}+y$ | -z) | 2.467 |
| -W(3) | | | 2.352 |
| -W(4) (2-x | $\frac{1}{2}+y$ | 1-z) | 2.381 |
| -O(3') (1-x | $-\frac{1}{2}+y$ | 1-z) | 2.354 |
| -O(6) | | | 2.559 |
| Na(2)-W(2) | | | 2.397 |
| -W(4) | | | 2.510 |
| -O(1) (1+x | y | z) | 2.383 |
| -O(2) | | | 2.322 |
| -O(6) (1-x | $-\frac{1}{2}+y$ | 1-z) | 2.355 |
| O(3')-Na(1)-W(1) | 100.1° | W(4)-Na(1)-W(2) | 78.1° |
| -W(2) | 92.6 | -W(3) | 90.6 |
| -W(3) | 98.7 | W(2)-Na(1)-W(3) | 167.5 |
| -W(4) | 170.7 | O(6)-Na(2)-W(2) | 92.7 |
| -O(6) | 92.6 | -W(4) | 93.0 |
| W(1)-Na(1)-W(2) | 101.4 | -O(1) | 92.2 |
| -W(3) | 82.0 | -O(2) | 103.4 |
| -W(4) | 82.2 | W(2)-Na(2)-W(4) | 77.8 |
| -O(6) | 169.5 | -O(1) | 146.7 |
| O(6)-Na(1)-W(2) | 86.3 | -O(2) | 108.8 |
| -W(3) | 89.0 | W(4)-Na(2)-O(1) | 68.9 |
| -W(4) | 92.6 | -O(2) | 161.9 |
| | | O(1)-Na(2)-O(2) | 102.5 |

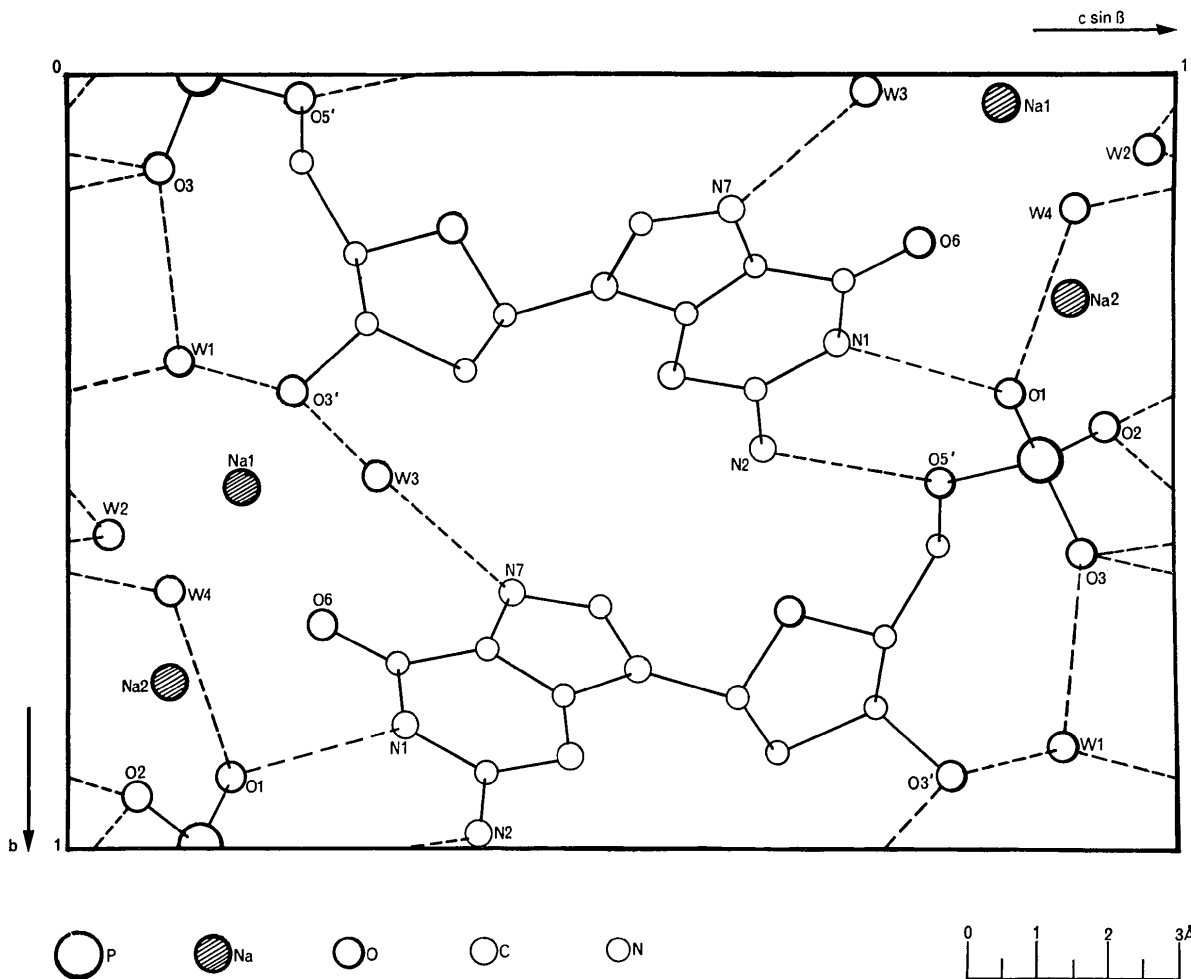


Fig. 3. A projection of the structure viewed along *a*. Hydrogen bonds are shown as broken lines.

Na(1). A similar difference in sodium ion coordination is found in the structure of disodium adenosine triphosphate (Kennard *et al.*, 1971).

Hydrogen-bonding scheme

Fig. 3 shows the content of the cell projected down *a*. The dashed lines indicate the probable hydrogen bonding scheme. Hydrogen-bond distances and angles are listed in Table 11. All these hydrogen bonds are reasonable except that possibly occurring between *W*(3) and *O*(3'). The *W*(3)–*O*(3') distance is 2.92 Å, but the angle *W*(3)–*H*(15)–*O*(3) is only 107.6°. The located position of *H*(15), however, is very reasonable since the angle *H*(15)–*W*(3)–*H*(16) is 100.4°. The contact between *W*(3) and *O*(3') also forms an edge of the Na(1) coordination octahedron and this may affect the situation. Apart from *H*(15), the only other hydrogen atom not involved in hydrogen bond formation is *H*(3) of the amide group. GDRP molecules are linked to each other by hydrogen bonds between *N*(1) and *O*(1), and *N*(2) and *O*(5'). There are no water–water hydrogen bonds.

Table 11. Hydrogen-bond lengths (Å) and angles (°)

| <i>X</i> — <i>H</i> ····· <i>Y</i> | <i>X</i> ··· <i>Y</i> | <i>X</i> — <i>H</i> ····· <i>Y</i> |
|---|-----------------------|------------------------------------|
| <i>N</i> (1)– <i>H</i> (1)····· <i>O</i> (1) ($-x \quad \frac{1}{2}+y \quad 1-z$) | 2.758 | 169.2 |
| <i>N</i> (2)– <i>H</i> (2)····· <i>O</i> (5') ($-x \quad \frac{1}{2}+y \quad 1-z$) | 2.961 | 171.2 |
| <i>O</i> (3')– <i>H</i> (9)····· <i>W</i> (1) ($1-x \quad \frac{1}{2}+y \quad 1-z$) | 2.741 | 164.7 |
| <i>W</i> (1)– <i>H</i> (10)····· <i>O</i> (3) ($-x \quad -\frac{1}{2}+y \quad 1-z$) | 2.726 | 147.3 |
| <i>W</i> (1)– <i>H</i> (11)····· <i>O</i> (2) ($x \quad y \quad 1+z$) | 2.767 | 172.2 |
| <i>W</i> (2)– <i>H</i> (12)····· <i>O</i> (2) ($1-x \quad -\frac{1}{2}+y \quad -z$) | 2.859 | 174.8 |
| <i>W</i> (2)– <i>H</i> (13)····· <i>O</i> (3) ($-x \quad -\frac{1}{2}+y \quad -z$) | 2.764 | 157.8 |
| <i>W</i> (3)– <i>H</i> (14)····· <i>N</i> (7) | 2.789 | 172.4 |
| <i>W</i> (3)– <i>H</i> (15)····· <i>O</i> (3') ($2-x \quad -\frac{1}{2}+y \quad 1-z$) | 2.921 | 107.6 |
| <i>W</i> (4)– <i>H</i> (17)····· <i>O</i> (1) ($1+x \quad y \quad z$) | 2.771 | 163.8 |
| <i>W</i> (4)– <i>H</i> (16)····· <i>O</i> (3) ($1-x \quad -\frac{1}{2}+y \quad -z$) | 2.783 | 175.1 |

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