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A Monte Carlo simulation study of the aqueous hydration of d(CGCGCG) in Z form

P. S. Subramanian and D. L. Beveridge

Chemistry Department, Hall-Atwater Laboratories, Wesleyan University, Middletown CT 06457, USA

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Summary. Monte Carlo computer simulation is described for the hexamer d(CGCGCG) in the Z form together with 910 water molecules at an environmental density of 1 gm/cc in a cubic cell under periodic boundary conditions. Water-water interactions were treated using the TIP4P potential and the solute water interactions by TIP4P spliced with the non-bonded interactions from the AMBER 3.0 force field. The simulation was subjected to proximity analysis to obtain solute coordination numbers and pair interaction energies for each solute atom. Hydration density distributions partitioned into contributions from the major groove, the minor groove, and the sugar-phosphate backbone were examined, and the probabilities of occurrence for one- and two-water bridges in the simulation were enumerated. The results are compared with observations of crystallographic ordered water sites from the X-ray diffraction studies.

Key words: Polynucleotides – Z form – Monte Carlo simulation

1. Introduction

Recent computer simulation studied reported from this laboratory have de[illegible] with various aspects of nucleic acid hydration, including the hydration [illegible] constituent base, sugar, and phosphate groups [1], the effect of hydration on the conformational stability of the phosphodiester group in water [2, 3, 4], and in preliminary form, studies of $d(CpG)_2$ in canonical A and B forms [5]. We have also reported studies on the hydration of dinucleotide duplex $r(GpC)_2$ [6], and $r(ApU)_2$ [7], and the dodecamer d(CGCGAATTCGCG) in the canonical A and B form [8, 9, 10]. The idea has been to proceed systematically through a well defined series of systems ranging from monomeric constituents to polymeric sequences, with a focus on developing as far as possible a structural chemistry of nucleic acid hydration based on calculated statistical indices of structure, and on the interpretation of more complex systems in terms of the results obtained for prototypes. Simultaneously the agreement obtained with experiment is documented to validate the calculation to the fullest possible extent.

We describe herein Monte Carlo computer simulation on the dilute aqueous solution of d(CGCGCG) in Z form at 250°C, analyze the results, and compare

calculated hydration with the available observed water positions in the d(CGCGCG) crystal. The structural chemistry of the hydration is described in terms of coordination number and pair interaction energy obtained from "proximity analysis" of the simulation [11, 12], and with calculated solvent density distribution [9]. A statistical analysis of the one-water and two-water bridges predicted by the simulation is also reported. The ordered water positions observed crystallographically is not yet fully reported and hence the comparison between the calculated result with the crystallographic sites is limited to the water molecules reported in the literature.

2. Background

In a series of experiments from the early 1970s, Pohl and Jovin [13] provided experimental evidence for the existence of poly(dC·dG) in two distinctly different conformations, one stable at low salt concentration and the other at high salt concentration. CD spectroscopy indicated the low salt form to be B-form DNA, whereas the CD was seen to be inverted for the high salt conformation. Crystallographic evidence for the nature of the high salt form was later provided by Wang et al. [14] based on studied of d(CGCGCG) and Drew et al. [15], who studied d(CGCG). The new conformation turned out to be a left-handed form of the double helix, characterized by a zig-zag geometry in the sugar-phosphate backbone. This conformation of DNA is now known as Z DNA, and is a left-handed duplex with 12 base pairs per turn of 44.6 Å. Z DNA has a sequence of alternating purine and pyrimidine residues with the purines in the *syn* conformation and pyrimidines in the *anti* conformation. In general, sequences containing CG base pairs have shown the ability to change to the Z conformation at high salt concentration, but AT sequences resist this transition. There have been found to be two Z conformations, ZI and ZII, which differ in the phosphodiester conformation, *gauche*(−) *trans* for ZI and *gauche*(+) *trans* for ZII. Our studies here are based on the more prevalent ZI form [16].

Though a variety of information exists regarding the structure of Z DNA [17] only limited information on the molecular nature of the hydration of the Z form of DNA is known. Wang et al. [14] reported a total of 62 solvent molecules in the crystal structure of d(CGCGCG), but the specific positions of these water molecules were not reported. They however pointed out the presence of a G-N2--W--O1P water bridge, which was speculated to be responsible for the stability of guanine in the *syn* conformation. In a later study on the crystal structure of d(m5CGTAm5CG), Wang et al. [18] observed the water molecules to be ordered around G-N2 and C-O2 sites but to be highly disordered near the AT base pairs. The G-N2--W--O1P bridge was observed again and the stability of guanine in *syn* conformation was attributed to it. Such a bridge is not possible for adenine, which lacks the amino group [14, 16, 18].

The minor groove of the Z hexamer has been shown to have a spine of water molecules which bridges the C-O2 site on adjacent base pairs. In the major groove the hydration is localized and restricted to one base site, G-N2. The anionic phosphate groups were also found to be fully hydrated, with 8–10 water molecules in the first hydration shell.

The motivation for the present calculation is mainly to obtain independent theoretical information on the hydration of the left handed DNA hexamer. The theoretical calculations of the hydration density via molecular simulation pro-

vides a prediction of the entire aqueous hydration complex of the DNA since the crystallographic ordered water positions are only a subset of the total hydration picture. The calculations, however, are subject to assumptions about the intermolecular force field and the distribution of counterions and it is of considerable interest to compare the experimental and theoretical results wherever possible in order to progress towards a more fully validated theoretical description of hydration.

3. Calculations

The calculations reported here are T, V, N ensemble Monte Carlo computer simulation on a system consisting of d(CGCGCG) in the Z form, based on coordinates obtained from the crystallographic data of Wang et al. [16], and 910 water molecules. The calculation was carried out for the hydrated hexanucleotide in a hexagonal prism cell treated under periodic boundary conditions. The volume of the system was chosen so as to give an overall density of 1 gm/cc and the temperature of the simulation was set to 298 K.

The configurational energies of the system were calculated under a pairwise interaction potential. Water-water interactions were computed using the TIP4P potential [19] and the solute-water interaction by TIP4P spliced with the Coulombic and van der Waals terms from the AMBER 3.0 force field of Weiner et al. [20]. Water-water interactions were restricted to a spherical shell of 7.5 Å. Solute-water interactions were treated under the minimum image convention. Electroneutrality of the system was established by uniformly scaling the nucleic acid charges in the manner previously used in our studies of the hydration of the B form of DNA [9].

The simulation was first allowed to proceed for 1500 K of equilibration followed by 1500 K of production. Force bias [21] and preferential sampling [22] were applied to accelerate the convergence. All calculations were carried out on CRAY XMP/48 supercomputer at sampling rate of 150 K/hr. Files were returned locally for display and analysis on a Evans and Sutherland PS350 color graphics unit using the molecular graphics program "DOCK" [23].

4. Results

The primary water coordination number of the DNA atoms calculated on the basis of proximity criteria are partitioned between minor groove, major groove and sugar-phosphate backbone and listed in Table 1. the primary coordination data gives 11.5 water molecules/nucleotide. The minor groove contributes about 1 water molecule/nucleotide or 2 per base pair implying that both the potential sites are hydrated. The primary coordination number of the major groove gives 3.3 water molecule per nucleotide. The first shell coordination of the backbone consists of contributions of 5.5 water molecule from each of the phosphate groups and 2.8 water molecules from the sugar moiety. The solute water binding energy, partitioned into contributions from minor groove, major groove and sugar phosphate backbone are listed in Table 1. The binding energy reported here is the interaction energy of the solvent molecules averaged over all the solute atoms.

Table 1. Coordination numbers and binding energies of Z d(CGCGCG)

	1° Coordination number	Binding energy (first shell) in kcal/mole
Minor groove	11	−6.38
Major groove	39	−4.43
Phosphate	54	−28.77[a], −2.65[b]
Sugar	34	−2.55[c]

[a] Free oxygens of phosphate group
[b] Ester oxygens of phosphate group
[c] Sugar O4′

The calculated hydration density is presented as superposition of 20 configurations collected at equal intervals from the Monte Carlo simulation in Figs. 1–6. The centers of mass of the water molecules are shown as black dots, and a representation of density is conveyed by the superposition of these positions. The important information obtained from these figures is the clustering of the points, which is proportional to the extent of localization of solvent density in a particular region.

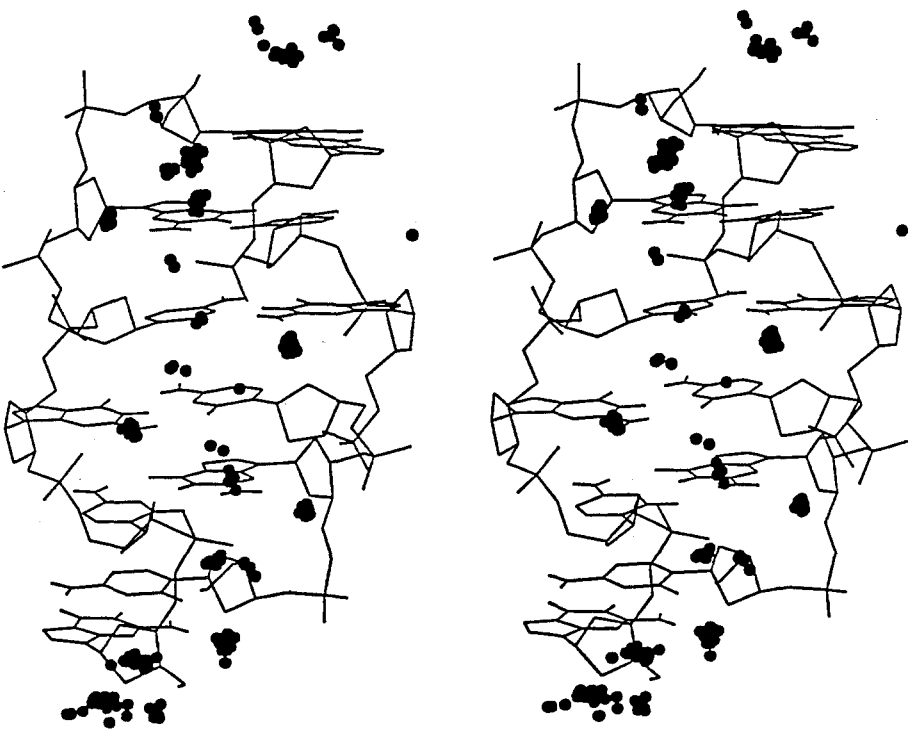

Fig. 1. Calculated first shell hydration density for the minor groove region of d(CGCGCG) in Z form.

The presence of hydrogen-bonded networks in the hydration can be seen from the analysis of the water structure in the individual configuration as shown. Though snapshots can be helpful in understanding the molecular structure of the complex hydration structure, a single structure is not representative of the ensemble and hence not too much should be inferred from them. A more statistical index is the calculated frequency of occurrence of one and two water bridges in the calculated hydration of the Z-DNA hexamer as given in Tables 2–4. The bridges are grouped into the categories interstrand, intrastrand-intraresidue and intrastrand-interresidue. The results are based on the analysis of the same 20 configurations used for the solent density plots. The main index of measuring bridges is the probability of occurrence, which is normalized to a probability of occurrence of one per configuration. A probability greater than unity implies more than one possibility of finding the bridge. Only those bridges which occur 10% of the time are listed.

The minor groove

Water molecules found in a given configuration within the first shell radii of N9, C4, N3, C2 and N2 of guanine and O2 and N1 of cytosine were assigned as the first coordination shell of minor groove. A second shell which is comprised of all

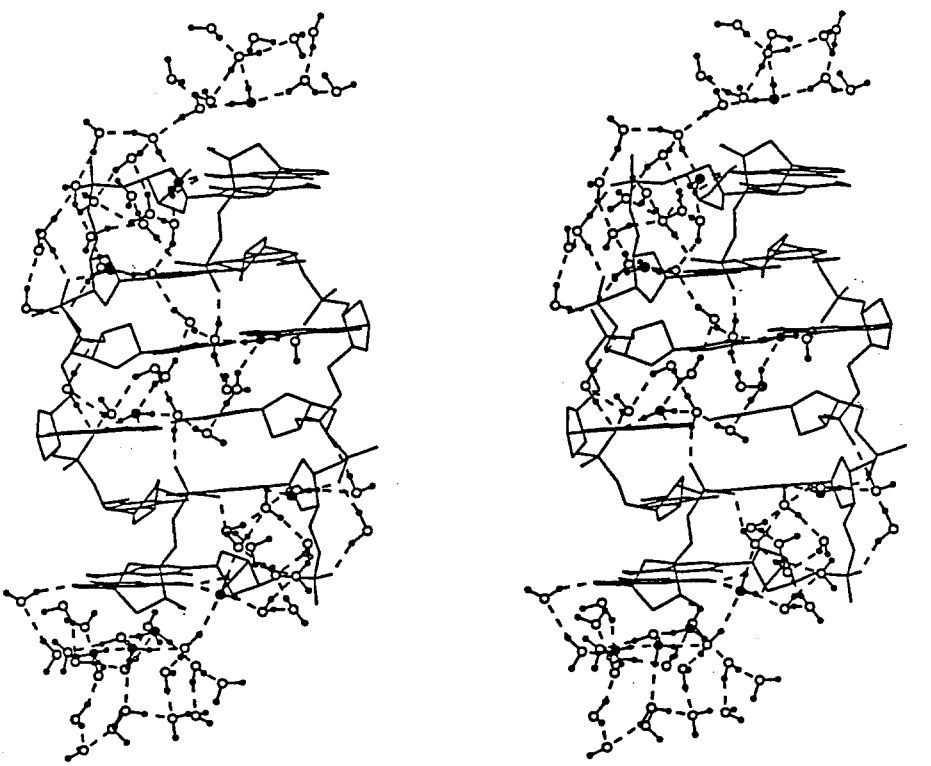

Fig. 2. A single configuration "snapshot" of a first shell hydration complex for the minor groove of d(CGCGCG).

the water molecules forming primary coordination to the first shell water molecules was defined to complete the definition of minor groove hydration. Proximity analysis turned out 71 water molecules in the minor groove, of which 11 are primary and 60 are secondary relative to the bases.

The calculated solvent density for the minor groove is shown in Fig. 1. There are two preferred sites of hydration, G-N2 and C-O2, of which G-N2 shows considerable localization compared to the C-O2 sites. The snapshot shown in Fig. 2 indicates a complex water network extending from one strand of the Z DNA duplex to the other. Similar water networks were also observed in the hydration studies of B DNA, but the filaments of waters crosslinking the strands were not so obvious. This may be due to the closer distance between the strands in the Z form as compared to in the B form. The CG region supports an ordered water network which spans the entire length of the hexamer. The preferred site in the calculation however comes out as G-N2, whereas the C-O2 sites are favored in the crystal studies.

The calculated one and two water bridges for the minor groove of the hexamer are given in Table 2.

Table 2. Water bridges observed in the minor groove of Z d(CGCGCG)
Only those bridges with a probability $\geqslant 0.1$ are listed

	Occupancy per configuration	Possible occurrences per configuration	Probability normalized to one occurrence per configuration
One water bridges:			
A. Interstrand bridges: None			
B. Intrastrand intraresidue bridges:			
CN1--W--CN3	0.75	6	0.13
GN2--W--O1P	3.90	4	0.98
CO2--W--O3′	0.95	6	0.16
GN9--W--O4′	1.20	6	0.20
C. Intrastrand interresidue bridges:			
CO2--W--GN2	1.75	10	0.17
Two water bridges:			
A. Interstrand bridges:			
CO2--W--W--CO2	0.75	5	0.15
CO2--W--W--GN2	1.00	6	0.17
B. Intrastrand intraresidue bridges:			
CO2--W--W--O1P	2.05	6	0.34
CO2--W--W--O3′	2.00	6	0.33
GN2--W--W--O1P	1.60	4	0.40
GN9--W--W--O4′	0.70	6	0.12
C. Intrastrand interresidue bridges:			
GN2--W--W--CO2	2.75	10	0.28
GN2--W--W--O3′	4.70	10	0.47
GN2--W--W--O1P	3.25	10	0.32
CO2--W--W--O1P	1.55	8	0.19

The major groove

Water molecules found within the first shell radii of N7, C5, C6, and O6 atoms of guanine and C4, C5, N4, and HN4 atoms of cytosine in a given configuration were assigned as the first coordination shell of major groove. Proximity analysis gave 39.4 water molecules in the primary coordination shell and 192 in the secondary shell.

The calculated solvent density for the major groove is shown in Fig. 3. The major groove of Z DNA is not a groove in the real sense, but is pushed to the surface of the duplex so much that it forms a convex bump compared with the usual concavity of a groove. The water molecules there are seen to be highly disordered in the simulation, with very little localization. The G-N7 shows out-of-plane hydration as in previous studies. The HN4 site is also hydrated.

The extent of water networking present in the major groove can be seen from Fig. 4. Being more exposed than in A or B form, the Z form in this region shows a myriad of networks involving first and second shell water. Collectively, they seem to form a sheath caging the major "groove" of Z DNA.

The calculated one and two water bridges in the major groove of the hexamer are shown in Table 3. Here again the one-water bridges are more in number than the two water bridges. The maximum probability for a one-water bridge is 38% for the intrastrand-interresidue bridge C-N4---W---G-N7. The intrastrand–intraresidue bridge G-N7---W---W---G-O6 occurs with 53% probability.

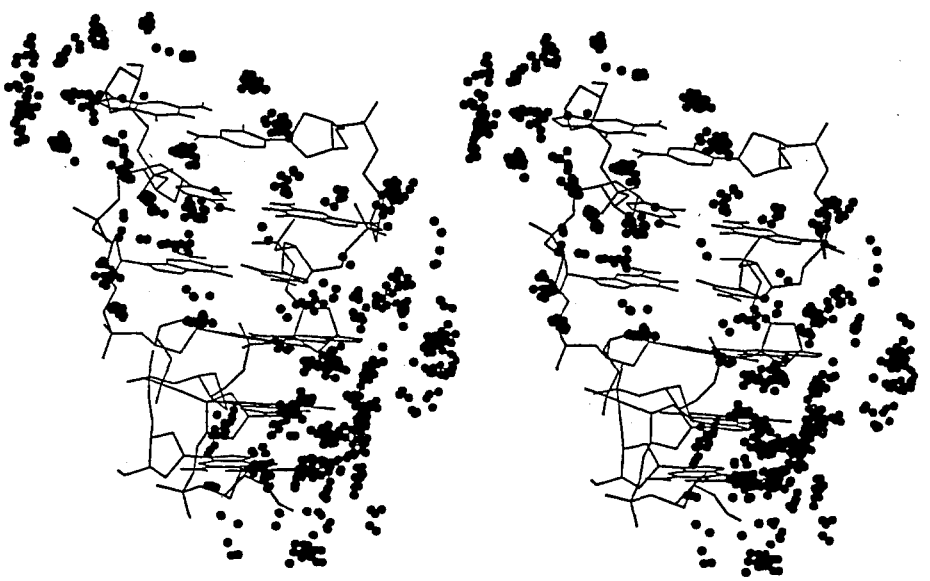

Fig. 3. Calculated first shell hydration density for the major groove region of d(CGCGCG) in Z form.

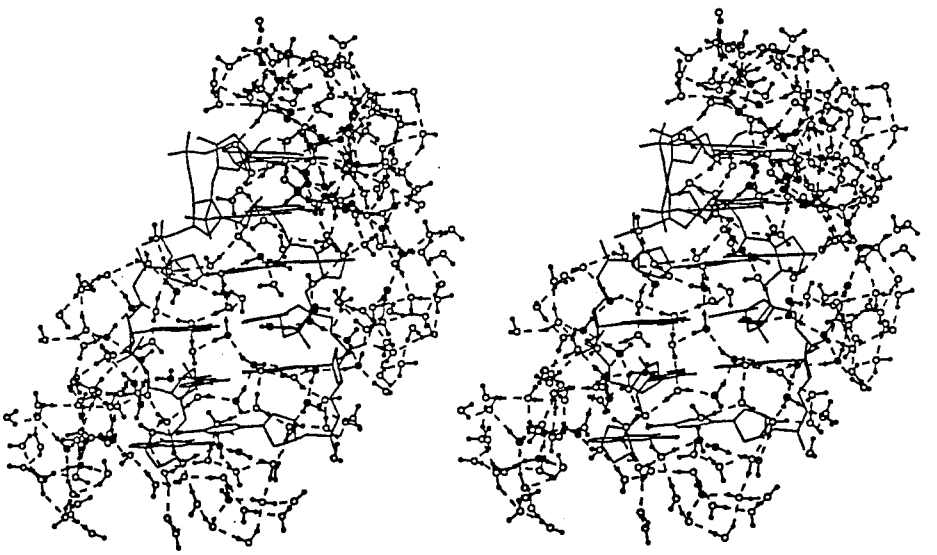

Fig. 4. A single configuration "snapshot" of a first shell hydration complex for the major groove of d(CGCGCG).

Table 3. Water bridges observed in the major groove of Z d(CGCGCG)
Only those bridges with a probability $\geqslant 0.1$ are listed

	Occupancy per configuration	Possible occurrences per configuration	Probability normalized to one occurrence per configuration
One water bridges:			
A. Interstrand bridges:			
GO6--W--CN4	0.60	6	0.10
B. Intrastrand intraresidue bridges:			
GO6--W--GN7	1.70	6	0.28
C. Intrastrand interresidue bridges:			
CN4--W--GN7	1.50	4	0.38
GO6--W--O5′	2.00	6	0.33
GN7--W--O5′	0.70	6	0.12
Two water bridges:			
A. Interstrand bridges:			
GO6--W--W--CN4	0.75	6	0.13
CN4--W--W--CN4	1.05	5	0.21
GO6--W--WGN7	0.45	4	0.11
B. Intrastrand intraresidue bridges:			
GN7--W--W--GO6	3.20	6	0.53
C. Intrastrand interresidue bridges:			
GN7--W--W--GO6	1.90	10	0.20
GO6--W--W--O5′	1.75	10	0.17

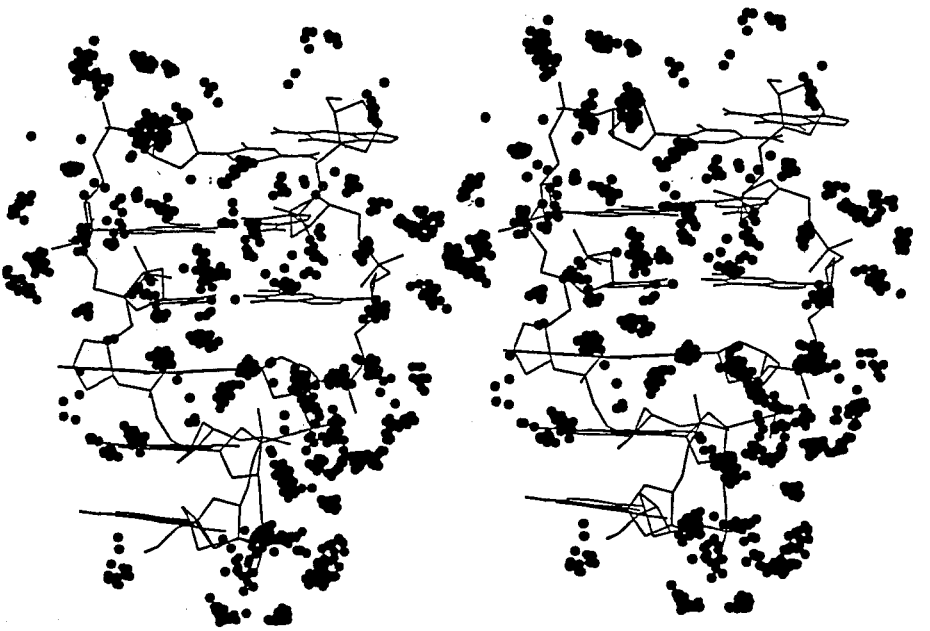

Fig. 5. Calculated first shell hydration density for the phosphate groups of d(CGCGCG) in Z form.

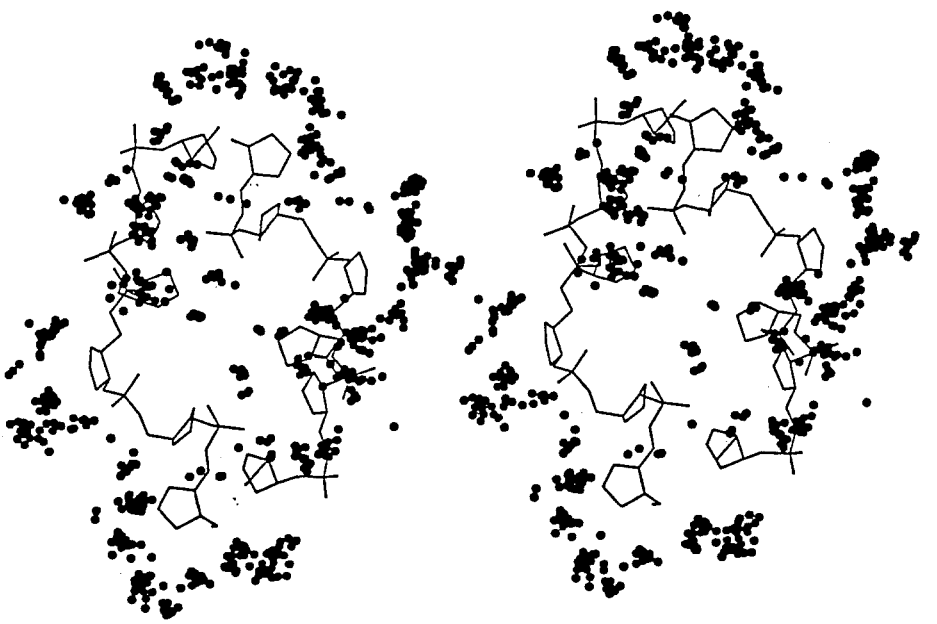

Fig. 6. Calculated first shell hydration density for the furanose sugar region of d(CGCGCG) in Z form.

Sugar-phosphate backbone

The calculated hydration density for the phosphate groups of the backbone is shown in Fig. 5. Here again as in B DNA considerable localization is evident, and concentrated in regions proximal to anionic oxygen. The ester oxygens seem to be competing unfavorably with the anionic oxygens. Proximity analysis reveals 33.9 water molecules for the first hydration shell of the sugar atoms (1.4 waters/nucleotide) and 55 water molecules for the phosphate groups. The primary coordination shell when converted to a per phosphate group basis gives 5.5 water molecule. This indicates that the "cones of hydration" as seen in other

Table 4. Water bridges observed in the backbone of Z d(CGCGCG)
Only those bridges with a probability $\geqslant 0.1$ are listed

	Occupancy per configuration	Possible occurrences per configuration	Probability normalized to one occurrence per configuration
One water bridges:			
A. Interstrand bridges:			
O1P--W--O1P	0.45	2	0.22
B. Intrastrand intraresidue bridges:			
O1P--W--O3′	2.45	10	0.25
O1P--W--O1P	2.90	10	0.29
O2P--W--O3′	5.85	10	0.58
C. Intrastrand interresidue bridges:			
O2P--W--O5′	1.50	10	0.15
O1P--W--O5′	1.15	10	0.11
O1P--W--O1P	2.35	4	0.59
O2P--W--O2P	0.55	4	0.14
Two water bridges:			
A. Interstrand bridges:			
O1P--W--W--O3′	1.30	8	0.16
O2P--W--W--O1P	1.40	4	0.35
O2P--W--WO3′	1.00	4	0.25
O1P--W--W--O1P	2.40	6	0.40
O3′--W--W--O3′	0.60	5	0.12
B. Intrastrand intraresidue bridges:			
O1P--W--W--O2P	7.45	10	0.75
O3′--W--W--O1P	2.70	10	0.27
O4′--W--W--O3′	1.25	12	0.10
O3′--W--W--O2P	4.15	10	0.42
C. Intrastrand interresidue bridges:			
O5′--W--W--O2P	2.50	14	0.18
O1P--W--WO2P	7.05	16	0.44
O1P--W--WO3′	3.75	18	0.21
O1P--W--WO5′	1.55	14	0.11
O1P--W--W--O1P	4.55	8	0.57
O2P--W--WO2P	2.85	8	0.36

systems essentially exist here as well, but a complete cone is formed only around one anionic oxygen. The anionic oxygen facing the groove, O2P, is close to the G-N2 or C-O2 and hence is not able to form a complete first shell cone as the water molecule which is first shell of G-N2 will be second shell for O2P.

The hydration density associated with the sugar atom is diffuse which seems to be typical of hydrophobic hydration (Fig. 6).

A compilation of one and two water bridges of the sugar-phosphate backbone atoms calculated for the hexamer from the 20 configurations is given in Table 4.

5. Discussion

Proximity analysis gives a total primary coordination number of 12 water molecules per nucleotide for this model of Z-DNA hydration. This is roughly two waters per nucleotide more than that calculated in the case of B DNA. The greater extent of hydration in Z form could be attributed to the exposed major groove in Z DNA. This result is similar to that reported by Clementi in B- and Z-DNA simulations [24].

Crystallographic studies have been carried out on the 5 Br cytosine derivatives of Z for CG hexamer [25], and a comparison between the crystallographically observed water sites and our calculated results is of interest even though the systems do not exactly correspond. The calculation gives an extended water filament in the minor groove region in which the water molecules are mostly hydrogen bonded to G-N2. The preferred site for this filament in the 5-Br crystal is however the C-O2. Previous calculations on $r(GpC)_2$ [6] and A and B forms [8] of DNA based on the AMBER/TIP4P force field have all shown the preference of the G-N2 over the C-O2 hydration site. The discrepancy between the observed and calculated results is likely to be force-field related.

The calculated hydration density in the major groove region is generally in agreement with that observed in the 5-Br crystallographic structure, with the hydration showing a preference for G-N7 over other sites. The major groove in the Z form is essentially nonexistent, and as a result the hydration here is highly disordered. The major groove sites are all individually saturated, with the water molecules forming a sheath covering the entire surface in the region of the exposed base-pair atoms.

The phosphate backbone shows the cone of hydration motif, with a coordination number of 5.5. Two complete cones do not form, since the minor groove atoms block one side of the anionic oxygen. In the crystal structure, the first shell hydration has a total of 8 to 10 water molecules.

The calculated coordination number for the first shell compared with the crystallographically observed sites of Westhof et al. [25] for the 5-Br Z-DNA hexamer is shown in Fig. 7. The comparison has to be made in the context that the calculated results are based on "full" hydration, whereas the observed sites are based only on the sites which turn out to be crystallographically ordered. The anionic phosphate oxygens, the G-N2, and the C-N4 sites are seen to be in close agreement with the crystal data.

Computation of frequently observed water bridges by Westhof gives yet another way of validating the calculated results. In the minor groove the single

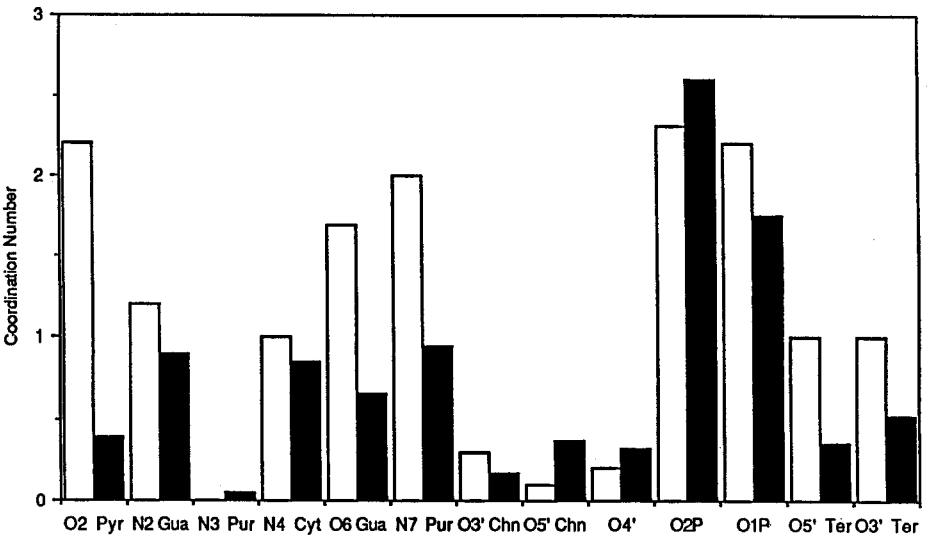

Fig. 7. Histogram of calculated (solid) and crystallographic (open) average water contacts for native Z form DNA. Experimental data from E. Westhof [25].

water bridge G-N2---W---O1P comes out with a probability of unity in the calculation. This bridge has been considered to stabilize the *syn* conformation of guanine, and thus to add to the stability of CG rich region in the Z form [18]. However, some of the bridges observed in the crystal do not turn up in the calculation. For example, in the backbone, the O1P---W---O1P bridge is seen in the crystal but the calculation picks up O1P---W---O1P in the intrastrand category.

The relative affinity of various sites in the Z form of the hexamer d(CGCGCG) has been worked out by Lavery and Pullman [26] by calculating electrostatic potential minima and steric accessibility. They find the major groove of Z DNA to have a lower (more negative) potential than the minor groove, and the free phosphate oxygens to have the lowest potential of all. In this calculation the solute-water binding energy can be used to compare the relative affinities. As seen from Table 1, the anionic phosphate comes out as the strongest binding site, followed by the major groove and the minor groove. The sugar O4′ and the ester oxygens of the phosphate group have the least binding energy and are comparable to that of the water-water binding energy. The order observed is similar to that observed in B DNA but the magnitudes are slightly higher for Z DNA. These results could also be highly dependent on the choice of potential functions.

In summary, the calculation supports an extended water network in the minor groove of the Z DNA as noted by crystal studies. The one water bridge G-N2---W---O1P also is seen to occur with a probability of unity. This bridge was also seen in the X-ray studies. The discrepancy between the experiment and theory is in the sites of the hydration in the minor groove. This site turns out as the C-O2 site in the crystal studies but the calculation repeatedly predicts the G-N2 site to be the favored site. The overall hydration pattern, however, agrees fairly well with the available crystal data.

6. Conclusions

The Monte Carlo simulations on d(CGCGCG) at 25°C reported herein have produced a detailed description of the aqueous hydration of d(CGCGCG) and delineated patterns in the hydration of the major groove region, minor groove region, sugars and phosphate groups of the molecule. The results are generally consistent with crystallographically observed water positions. The calculation showed the presence of a 'spine of hydration' in the minor groove linking the G-N2 sites on the adjacent base pairs. The 'spine of hydration' was observed in the crystal structure, but involved the C-O2 sites on the adjacent base pairs. The water bridge G-N2---W---O1P, considered to stabilize the *syn* conformation of guanine was observed in the calculation to occur with a probability of unity in the calculation, i.e., every possible occurrence of the bridge is satisfied. Future studies must pursue the relationship of water bridges to the thermodynamic stability of the system. A subsequent point of interest is the sensitivity of the results presented here to the choice of intermolecular potentials and to the modeling of electrostatics in nucleic acid systems.

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References

1. Beveridge DL, Mezei M, Mehrotra PK, Marchese FT, Vasu TR, Ravishanker G (1984) J Biomol St Dyn 2:261
2. Jayaram, B Mezei M, Beveridge DL (1987) J Comp Chem 8:917
3. Jayaram B, Mezei M, Beveridge DL (1988) J Am Chem Soc 110:1691
4. Jayaram B, Ravishanker G, Beveridge DL (1988) J Phys Chem 92:1032
5. Howell PL (1986) Ph.D. Thesis, Birkbeck College, University of London
6. Subramanian PS, Pitchumani S, Beveridge D.L., Berman HM (1990) Biopolymers 29:771
7. Subramanian PS, Beveridge DL, Berman HM (in preparation)
8. Subramanian PS, Beveridge DL (1989) J Biomol St Dyn 6(6):1093
9. Subramanian PS, Ravishanker G, Beveridge DL (1988) PNAS USA 85:1836
10 Subramanian PS, Swaminathan S, Beveridge DL (1990) J Biomol St Dyn 7:1161
11 Mezei M, Beveridge DL (1986) Methods in Enzymology 127:21
12 Mehrotra PK, Beveridge DL (1980) J Am Chem Soc 102:4287
13 Pohl FM, Jovin TM (1972) J Mol Biol 67:375
14 Wang AHJ, Quigley GJ, Kolpate FJ, Crawford JL, van Boom JH, van der Marel G, Rich A (1979) Nature, London 282:680
15 Drew HR, Dickerson RE, Itakura K (1978) J Mol Biol 125:535
16 Want AH, Quigely GJ, Kolpak FL, van der Marel G, van Boom JH, Rich A (1981) Science 211: 171
17 Rich A, Nordheim A, Want AH (1984) Ann Rev Biochem 53:791
18 Wang AH, Hakoshima T, van der Marel G, van Boom JH, Rich A (1984) Cell 37:321
19 Jorgensen WL, Chandrasekar J, Maduar J, Impey R, Klein ML (1983) J Chem Phys 79:926
20 Weiner SJ, Kollman PA, Case DA, Singh UD, Ghio C, Alagona G, Profeta S, Weiner P (1984) J Am Chem Soc 106:765
21 Pangali C, Rao M, Berne BJ (1978) Chem Phys Lett 55:413
22 Owicki J, Scheraga HA (1979) Chem Phys Lett 47:600
23 Manion F, Norman E, Stodola B, Wood B (1988) DOCK
24 Swamy K, Clementi E (1987) Biopolymers 26:1901
25 Westhof E (1987) Int J Biol Macromol 9:186
26 Lavery R, Pullman A, Pullman B (1982) Theoret Chim Acta 62:93