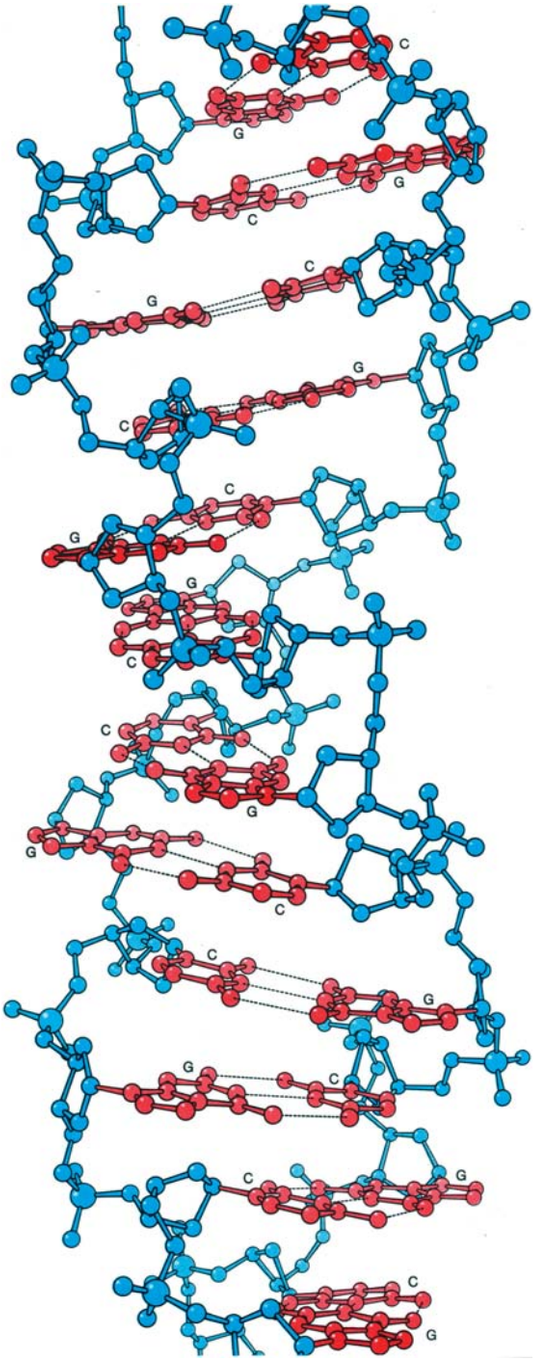

Fig. 23.3.1.4. Infinite Z-DNA helix, generated as before from the central four base pairs of the hexamer C-G-C-G-C-G (Z1). G and C bases alternate along each chain. The sugar–phosphate backbone adopts a pronounced zigzag pathway, rising vertically past each guanine, but travelling horizontally across the helix at cytosines. Hence, the formal helix repeat is two base pairs, G followed by C, rather than a single base pair, as in the A and B helices. Note that the structures of Z-DNA and A-DNA are in many ways the inverse of one another. The Z helix is left-handed, tall and slim, with a deep minor groove, a flattened major groove and small propeller twist. The A helix is right handed, short and broad, with a deep major groove, a shallow minor groove and large propeller twist. (From Dickerson, 1983.) Reprinted courtesy of the estate of Irving Geis. Rights owned by Howard Hughes Medical Institute.

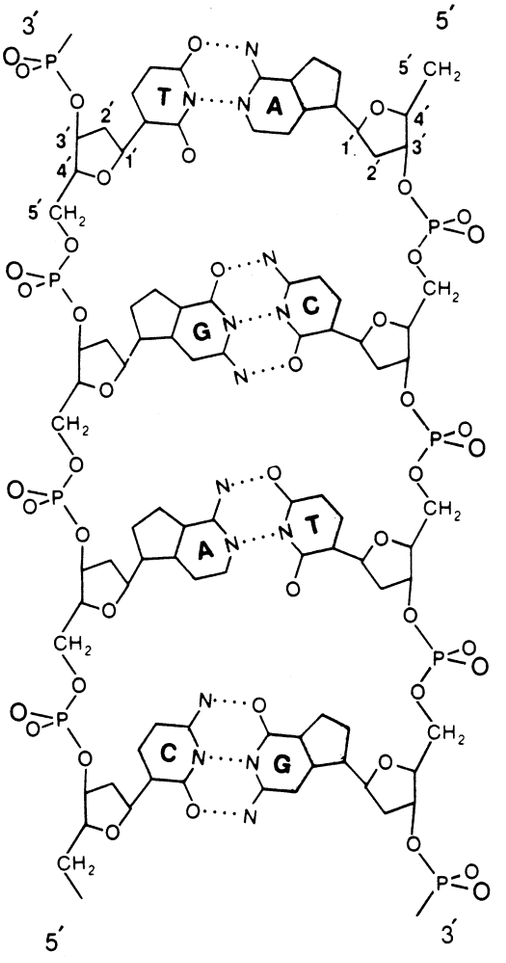

Fig. 23.3.2.1. Unrolled schematic of A- or B-DNA, viewed into the minor groove. Paired bases are attached to backbone chains that run in opposite directions: downward on the right and upward on the left. Z-DNA differs from A- and B-DNA in that the two backbone chains run in opposite directions from those shown here. Hence, Z-DNA cannot be obtained from A- or B-DNA by simple twisting around the helix axis.

Other related but nonstandard base pairs are compared in Fig. 23.3.2.8. Inosine (I) is useful in studying properties of DNA in that, when paired with cytosine (C), it creates a G·C-family base pair having overall similarity to A·T. Similarly, diaminopurine (DAP) [also known as 2-aminoadenine (2aA)], when paired with thymine (T), creates a G·C-like pair from A·T-family bases. Hence, in a given experimental situation, one can unscramble the relative significance of number of hydrogen bonds *versus* identity and location of exocyclic groups.

The conventional Watson–Crick base pairing of Fig. 23.3.2.7 uses the hexamer 'end' of the purine base. A different type of base pairing was proposed many years ago by Hoogsteen (1963), in which the upper edge of the purine was used: N7 and N6/O6. Hoogsteen base pairing is shown between the left-hand two bases in each part of Fig. 23.3.2.9. Note that in Hoogsteen base pairing of A and T, each ring provides both a hydrogen-bond donor and an acceptor. Guanine cannot do this, since both its N7 and O6 positions are acceptors. As a consequence, in a G·C pair, C must supply both of the hydrogen-bond donors. It can only form a Hoogsteen base pair with G when the cytosine ring is protonated. This would lead one to expect triplex formation only at low pH. However, the stability of a triplex can, to a certain extent, alter the pK_a of the N—H proton itself. (Recall the shift in pK_a of buried Asp and His

references