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Metal binding induces conversion of B- to the hybrid B–Z-form in natural DNA

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ABSTRACT

Highly polymerized herring testis DNA of the random nucleotide sequence has been studied in soluti by circular dichroism and ultra-violet absorption spectrometry under various experimental conditio At low temperature upon addition of 0.05 M NaCl or 1.15 M $MgSO_4$ the DNA formed a helix that belong to the B-family. As the temperature was increased a transition from the pure B- to the hybrid B–Z-fo occurred in the presence of 1.15 M $MgSO_4$. This transition occurred over a large range of temperatu and corresponded to a non-cooperative conformational change. A similar DNA transition was induc with 0.098 mM $Co(NH_3)_6Cl_3$. However, in the presence of 5.3 M NaCl the DNA conformation was similar to that observed in 1.15 M $MgSO_4$ or 0.098 mM $Co(NH_3)_6Cl_3$ independently on the environmen temperature. In 5.3 M NaCl the DNA is thought to undergo a transition from one to another right-hand conformation that could be intermediate partially dehydrated conformer arising on the first step in t sequential transition to the dehydration of the polynucleotide. Our results show that a realistic model native DNA, bearing Z-tracts embedded in B-helixes, can be obtained upon binding of alkaline earth transition metals.

1. Introduction

Induced with salt or ethanol solutions DNA transition from the right-handed B-form to the left-handed Z-helices was first shown in 1970 by drastic circular dichroism (CD) changes [1–3]. Further examination of this phenomenon showed that all strictly alternating purine/pyrimidine duplex helices could undergo this order/order transition from the right-handed to the left-handed helix under suitable experimental conditions [1,4–8]. For example, poly-d(G–C) duplexes, widely studied in different laboratories, were found to fold into a Z-helix in both fibers [9,10] and in solution [1] upon reducing water activity and crystallization of DNA. Poly-d(A–T), and poly-d(A–C) · poly-d(G–T) can also convert from B- into Z-helix. However, the conditions of both those conversions and the conversion of poly-d(G–C) duplexes differed markedly and were shown to depend on the energetic cost of the B- to Z-helix transition in these sequences of differing composition [8,11–14]. The modification of deoxyguanosine- or deoxycytidine residues with iodine, bromine and to a lesser extent methyl can significantly facilitate the purine/pyrimidine sequences to adopt Z-type conformations [1 For instance poly-(dG–m^5dC) was found to undergo a B- to Z-he transition at close to physiological ionic strength [7,15].

The phenomenon of the B- to the Z-helix transition of DNA h been mainly studied on short pieces, poly- or oligodeoxynucleoti fragments, with strictly alternating purine/pyrimidine sequenc Similar studies of the molecules containing fragments of both alt nating purine/pyrimidine sequences and the random nucleoti composition are not so thorough. Only a few papers provide da on conversion of synthetic deoxyoligonucleotides from the pu right-handed B-form to the hybrid B–Z-form [11,16–20]. It is not worthy that all these studied molecules contained at least h poly-d(G–C) stretches. Similar studies of highly polymerized nat ral DNA, containing random nucleotide sequences, have not be undertaken. However, the current knowledge allows us to assu that within the same molecule of natural DNA, radically differe geometries may coexist. This assumption is confirmed by Kim al. [16] who showed $d(G–C)_n$ sequences may transiently exist solution as Z-conformation embedded in linear B-DNA. The hybr B–Z-form of DNA containing left-handed regions separated by B–Z junction from right-handed regions is believed to exist in vi and fulfill various roles in nature. Although the potential Z-DN forming sequences within natural genomic DNA are short, the Z-helix segments can play a regulatory role in gene expression a

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