Macromolecular polarities

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III. MACROMOLECULAR POLARITIES

A. FREE MACROMOLECULES

Both α-helical and β-sheet tertiary conformations of proteins involve intra- and inter-hydrogen (H) bonds and the specificity of base pairing in nucleic acids is also determined by H bonds.

1. NUCLEICS ACIDS

a) Deoxyribonucleic acid (DNA)

DNA strands carry information encoded in the sequence of the H bonded bases, which can be considered as analogous to bits in a computer code.

a^1 *Structure*

The asymmetric location of base pairs in the B form of DNA (see **I**) creates a smaller minor groove and a larger major groove in the double helix. There are two major structural motifs, the helix-turn-helix and zinc finger and many DNA-binding proteins contain either of them (Schleif, 1988).

The double-DNA has been mimicked by self- assembly of the helices achieved in the presence of Cu^{+1} ions (Koert *et al.*, 1990). Many DNA-binding proteins recognize specific sites through small, discrete domains which reveal a variety of different designs folded to contact DNA base pairs in the major groove through hydrogen bonds, both direct and water-mediated, and non-polar van der Waals interactions (Harrison, 1991).

a^2 *Replication*

DNA and RNA are not the only possible replicators. Indeed, and as an aspect of self-organization in the perspective to unravel the origin of life, Rebek's (1992) recent test-tube replicators use as DNA itself H bonding as structural information. In Rebek's system, the product of pairing of an imide-ester and an adenine-containing amine is replicated by serving as template on which a new ester-amine pair lines up guided by H bonds. However, the holy grail remains to combine informational content with replication (Orgel, 1992).

Interestingly, the nucleoskeleton is implicated in the topology of replication (Cook, 1991). As for the current eucaryotic model of asymmetric DNA replication fork involving DNA polymerases for replication of both DNA strands according to the 5'-to-3' directionality rule, it is discussed by Hübscher and Thömmes (1992).

a^3 *Transcription*

Transcription factors interact with *cis*-acting control elements present in both nearby promotors and remote enhancers (Maire *et al.*, 1989). A protein-mediated joining of distant recombination sites at the enhancer has been termed the invertasome. This Hin protein "binds to two *cis*-acting recombination sites and catalyzes a site-specific DNA inversion reaction that regulates the expression of flagellin genes in *Salmonella*" (Heichman and Johnson, 1990). Little is known about the *trans*-active factors which control the *cis*-acting signals involved in the transcriptional activation of the interleukin (IL-2) gene. Cell type-specific *trans*-active proteins have been assayed in the *Xenopus* oocyte (Rungger *et al.*, 1990).

a^4 *Mutations*

H bonds are "ideal template forces for they are highly specific, unlike the van der Waals interactions" (Watson, 1970). Mistakes in such bonding during DNA replication lead to mutagenic replacement of a single base pair by another.

DNA strand asymmetry might be reflected in an inequality in the mutation rates of its two strands (Wu and Maeda, 1987, in Wu, 1991).

In polar mutants, ribosomes carrying nascent peptide chains are released as they encounter the nonsense codon in the messenger RNA of the mutated gene. This causes the mRNA distal to the mutation to remain "naked", i.e. not covered with ribosomes, a condition in which it seems to be highly susceptible to endonucleolytic attack (Hansen *et al.*, 1973 in **III**).

b) Ribonucleic acid (RNA)

Transfer RNAs (tRNAs) have a high net negative charge. A "hole" in the potential surface has been found in the anticodon region of the elongator tRNAs. Consequently, the anticodon region is the least negative, or conversely the most positive, region of the molecule. This may have implications in the ability of tRNAs to associate with other negatively charged macromolecules, in particular mRNA. This hole which is not found when simple Coulombic potentials are used is due "both to the structure of the elongator tRNA anticodon loops and to the different polarizabilities of the solvent and tRNA" (Sharp *et al.*, 1990).

Anti-sense RNA has been produced in a plasmid vector to study animal development (Rungger *et al.*, 1990). Self-splicing or catalytic introns have been assumed to fulfil protomotion of efficient *cis*- and *trans* splicing of RNA (Sharp, 1991). A short RNA molecule and six proteins are the components of the signal recognition particle (SRP) which helps proteins destined for export from the cell (Hann and Walter, 1991).

2. PROTEINS

Protein folding in vitro is a spontaneous process dictated primarily by the linear sequence of amino acids (Anfinsen, 1973). However, the problem of how a protein is folded in its tertiary structure cannot yet be predicted from its amino acid sequence. Preliminary structural assignments for the catalytic domain of protein kinases have been made by Benner and Gerloff (1990). The hydrophobic effect has been considered as the major factor in stabilizing such folded structures of globular proteins (Dill, 1990). Coiled coils formed by two or three α helices in parallel can be predicted from protein sequences (Lupas *et al.*, 1991).

Chaperones stabilize unfolded or partially folded structures and seem to act as molecular detergents, primarily by preventing partially folded and unassembled protein subunits from aggregating and precipitating (Creighton, 1991; Gething and Sambrook, 1992). Heat-shock proteins play a role as molecular chaperones and so-called "protein chaotropes" might represent the trigger of the stress response (Welch, 1991).

The importance of polar substituants in the execution of organic synthesis has been surveyed by Tse-Lok Ho (1991) which emphasizes the use of the polarity of alternation rule as a framework for analysis.

6. ANTIGENS-ANTIBODIES

The mechanism for their recognition involves not only hydrogen bonding, van der Waals contacts, salt bridges, and buried surface area but conformational changes in which peptide binding is replaced by an alternative hydrogen bond (Rini *et al.*, 1992).

7. SYNTHETIC POLYMERS

The principle of a light-harvesting "antenna" complex directing excitation to a semiconductor-based photosynthetic system has now been used to create a new type of solar cell (0'Regan and Grätzel, 1991).

B. AGGREGATES

1. Crystals and quasicrystals

By contrast with the disordered patterns of quasicrystals (three dimensional disordered structures, Shechtman *et al.*, 1984), crystals are arrays of molecules ordered through repetition of unit cells which enclose themselves a set of asymmetric units defined by the space group (see McPherson, 1989). They acquire isotropic heterogeneities during growth as a result of differences in surface structure. Sector zoning or anisotropic segregation of chemical elements (Mn^{2+}, Fe^{3+}, etc.) can be displayed by calcite crystals and associated with ordering and local reduction of symmetry (Dickson, 1991). However, the distinction between "crystals" and "quasicrystals" appears now artificial and might have to be abolished as proposed by D. Mermin in a recent review book (DiVincenzo and Steinhardt, 1991).

Special attention will be devoted these next years to the so-called smart molecules which include piezoelectric ceramics, crystalline materials with electrical polarity (lead zirconium titanate, etc.) that quickly translate pressure or vibration into an electric current and vice versa. Otherwise, electrorheological fluids contain polarizable particles which can align themselves into filaments under the influence of an electric field thereby changing the material from a liquid to a near-solid (see Hoke, 1992).