ribose ring in RNA is not planar but puckered such that C-3' is about 0.5 Å away from the plane through the other four atoms and on the same side as C-5', which is called the C-3'-endo envelope form. The conformation about the C-5'-C-4' bond is such that O-5' is located 'above' the ribose ring. The conformation of the phosphodiester group is *trans* about the C-5'-O-5' bond and *gauche* (approx. 300°) about the O-5'-P and P-O-3' bonds, and the torsional angle about the C-3'-O-3' bond is close to 200° with respect to C-4'.

The base pairs in natural RNA are of the Watson-Crick type and arranged such that their planes are tilted by about 76° with respect to the axis of the double helix with a pitch height of 11 base pairs or 30.9 Å (in A-RNA).

One may assume that in double-helical regions of the tRNA molecule structural parameters similar to those described above are valid. In the loop regions, however, the conformational parameters obtained for monomer nucleosides, which are different in some instances, might be more relevant. Thus the 'rare' tRNA nucleosides 4-thiouridine (Saenger & Scheit, 1970) and inosine (Thewalt, Bugg & Marsh, 1970) were found to crystallize in the unusual *syn* conformation with O-2 and C-4 respectively 'above' the ribose residue. It was established for crystalline dihydrouridine (Saenger & Suck, 1971; Sundaralingam, Rao & Abola, 1971) that the base is puckered because of the saturated C-5-C-6 bond, that the sugar conformation is C-2'-endo and that O-5' is not positioned 'above' the ribose ring. The conformation of the phosphate group was found to differ by 180° or 120° in some nucleotides from the one described for RNA. Further, base pairs other than the Watson-Crick type have been observed for co-crystallized nucleosides or bases

that might be involved when inter-loop base-pairing occurs.

Conformation of tRNA species. From biochemical, chemical and physicochemical experiments, structures for tRNA have been proposed. All of these proposals use the cloverleaf structure as a basic element. The arms of the cloverleaf can be folded in various ways (Cramer, 1971). The final answer on the tertiary structure of tRNA can only come from X-ray-diffraction studies on single crystals, which are now available. In any case, the arrangement must fulfil the specifications of optimum conformational arrangement in the mononucleotide moieties of the macromolecule. A computable optimization has been made for the tRNA conformation that folds together with -C-C-A arm, the dihydrouridine arm and the T-ψ arm (Cramer, Doepner, von der Haar, Schlimme & Seidel, 1968). The structure comprises a long helical stack from the -C-C-A end to the anticodon loop, involving 22 stacked bases. This gives the molecule a length of approx. 70 Å. Such a structure can be built for any of the known sequences of tRNA.

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COMMUNICATIONS

The Combination of Nuclear-Magnetic-Resonance Spectroscopy and Potential-Energy Calculations in the Study of Peptide Conformation in Solution

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N.m.r. spectroscopy can give detailed information about the backbone conformation of peptides in solution. This use of n.m.r. is based on the fact that the magnitude of the spin-spin coupling between the peptide NH and the neighbouring α-CH protons is related to the dihedral angle, ϕ , of the HN-α-CH fragment. Because of the $\cos^2 \phi$

form of the relationship, a given value of the spin-spin coupling constant, J_{NC} , may correspond to more than one value of ϕ . In many cases this ambiguity can be removed by eliminating those values of ϕ that are sterically forbidden, as indicated by 'hard-sphere' calculations (see Ramachandran & Sasisekharan, 1968). Further, the population distribution as a function of ϕ and ψ (the α-CH-CO dihedral angle) predicted from potential-energy calculations (Scott & Scheraga, 1966; Brant, Miller & Flory, 1967; Ramachandran, Venkatachalam & Krimm, 1966) can be used to calculate a predicted value of J_{NC} . This can provide a useful experimental criterion by which to judge the applicability of a given potential-energy map to a particular system.

This approach will be illustrated by studies of some component peptides of gastrin: Asp-Phe,

Met-Asp-Phe, Trp-Met-Asp-Phe and β -Ala-Trp-Met-Asp-Phe. These peptides seem to exist in a relatively narrow range of conformational populations centred around $\phi = 95^\circ$, and the population distribution is described quite well by the potential-energy map given by Scott & Scheraga (1966). This series of peptides will also be used to show how n.m.r. can give precise information on the populations of the different rotamers about the side-chain α -CH- β -CH₂ bond, and finally a possible method by which n.m.r. may be able to give information about the other backbone dihedral angle, ψ , will be discussed.

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Conformations of Crystalline Alginic Acids and their Salts

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The physical properties of alginates, e.g. viscosity, gel formation, ion-selectivity etc., are known to be dependent on the proportions of mannuronic acid and guluronic acid in a given sample (Smidsrød & Haug, 1968), but the relationships between these properties and the molecular structures of alginates are poorly understood.

In the partially crystalline fibrous form, poly- β -D-mannuronic acid and poly- α -L-guluronic acid are stereochemically very different (Atkins, Mackie, Parker & Smolko, 1971). Polymannuronic acid is a flat ribbon-like chain whose molecular repeat of 10.3 Å contains two diequatorially (1eq,4eq)-linked β -D-mannuronic acid units in the C1 chair form. In contrast, polyguluronic acid has a repeat of 8.7 Å also containing two α -L-guluronic acid units, but in the 1C chair form. Thus the sugar units are diaxially (1ax,4ax)-linked and the chain has a rod-like conformation.

The study of oriented specimens of salts of these substances by X-ray diffraction has revealed some other interesting differences. In the polymannuronates (lithium, sodium, potassium and calcium salts) the fibre repeating value is about 15 Å. The chain is now a helix, though still close to maximum extension, in which one turn contains three monosaccharide units in the C1 chair. These structures are reminiscent of β -(1 $\rightarrow$ 4)-linked xylan, which also has three D-xylose units in a repeat of 14.8 Å

(Marchessault & Sarko, 1967). In contrast, the X-ray-diffraction photographs of ammonium polyguluronate and potassium polyguluronate clearly show that the twofold repeat of 8.7 Å (and therefore the 1C chair) is maintained in these structures. The X-ray-diffraction photographs of other salts (including the calcium salt) are poorly resolved at present, but these show the same general features of the ammonium and potassium salts. It is therefore to be expected that they too have the sugar units in the 1C chair form and similar overall chain conformations. The results also provide evidence that polymannuronate may be a more flexible structure than polyguluronate, in the sense that rotations can occur about the glycosidic bonds in the former, whereas the units are more rigidly held in potassium polyguluronate chains. [The related substance polygalacturonate is similar to polyguluronate in having (1ax,4ax)-linked units, but is also like polymannuronate in having three sugar units in a molecular repeat of 13 Å.]

Alginates may serve as ion-exchangers and structural materials in the natural state, and it is thought that they are largely co-polymers made up of blocks of the type $(-M-)_n$, $(-G-)_n$ and $(-M-G-)_n$ (where M is mannuronic acid and G is guluronic acid) (Haug, Larsen & Smidsrød, 1966) whose proportions may vary according to the physical requirements of particular tissues in particular environments. In a qualitative sense it is noteworthy that alginates enriched in $(-M-)_n$ appear to be characteristic of more flexible tissues, whereas those enriched in $(-G-)_n$ are found in tissues (such as cell walls) that require more rigidity (Frei & Preston, 1962).

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The Conformation of Polygalacturonic Acid Subunits

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Several workers have employed computational methods to obtain an estimate of the energy of a disaccharide as a function of the two angles of