Helix Formation by Guanosine-5′ Phosphate

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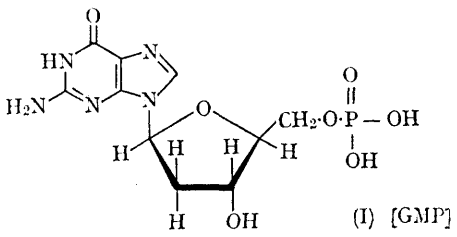
IT has long been known[1] that concentrated aqueous solutions of guanylic acid form a gel on cooling, and more recently it has been shown[2] that the 5′-isomer (I) is particularly prone to aggregation. Solutions (10^{-2} M) of guanosine-5′ phosphate (GMP) at high ionic strength are viscous[3] and exhibit hypochroism and an enhanced optical rotation.[2] The *X*-ray-diffraction patterns of fibres drawn from the viscous solution indicate[2] that the aggregate is either a card-pack polymer of layered structures formed by the hydrogen-bonding of four guanine residues or a continuous helix with four residues per turn and a pitch of 3·36 Å.

It is now found that concentrated aqueous solutions of GMP (I) near to 0° exhibit a strong circular dichroism which decreases as the polymer dissociates thermally (Figure). The optical activity of the monomer is small, and the circular dichroism recorded (Figure) arises from the coupling between the electric dipole transition moments of neighbouring guanine residues in the polymer. Current theories[4,5] of the optical rotatory power of helical polymers distinguish two types of coupling which are dependent on the pitch and on the radius of the helix, respectively. For each type of coupling the circular dichroism is expected to consist of two bands, or groups of bands, with equal areas

and opposed sign, as is observed in the present case (Figure). The two types differ, however, in that the pitch-dependent coupling modes give rise



(I) [GMP]

only to resultant electronic transitions which are polarised perpendicular to the fibre axis of the helical polymer, whereas the radius-dependent coupling modes give transitions polarised both parallel and perpendicular to the helix axis.[4,5] Only pitch-dependent coupling modes are possible in the card-pack polymer of GMP consisting of layers of discrete tetrameric guanylic acid units, but both pitch- and radius-dependent coupling modes contribute to the rotatory power of a continuous helical chain of hydrogen-bonded guanine residues.

The plane-polarised absorption spectra of orientated films of the GMP polymer, produced by stroking the thixotropic gel with a glass slide, indicate that the 2520 Å polymer band is polarised parallel to the fibre axis along the direction of stroking. Accordingly the associated 2440 Å circular dichroism band of the GMP polymer is due to a radius-dependent coupling mode, and the polymer consists of a continuous helix of guanine residues and not a layered aggregate. Since the parallel-polarised circular dichroism band is positive in sign, the helix of guanine bases is right-handed.

The formation of the GMP polymer is favoured by a high ionic strength[2,3] of a uni-univalent electrolyte (0·5 M-sodium chloride), but it is inhibited by magnesium chloride at the same concentration. However, a low concentration of magnesium chloride (GMP/Mg^{2+} = 2) produces a polymer with modified optical properties (Figure). The hypochromism of the isotropic absorption is less marked, suggesting that the guanine bases have a larger spacing in the polymer containing magnesium ions, whilst the circular dichroism is

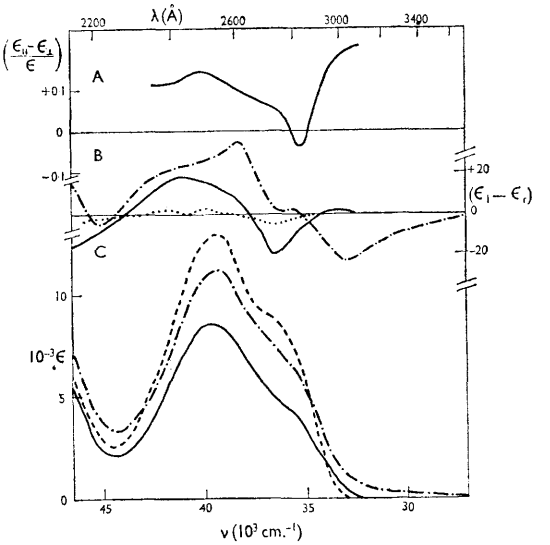


FIGURE: *The optical properties of guanosine-5′ phosphate* (I); (A) *the relative extinction coefficients of an orientated film of the GMP polymer for light polarised parallel* (∥) *and perpendicular* (⊥) *to the fibre axis; and* (B) *the circular dichroism, and* (C) *the isotropic absorption spectra of GMP in aqueous solution at an ionic strength made up to* 0·55 M *with sodium chloride: monomer* (3·4 × 10^{-4} M) — — — —; *and polymer* (2·1 × 10^{-2} M) ——— *at* 1°; ..... *at* 20°; *and* —·—·—·— *at* 1° *with magnesium chloride* (*GMP*/Mg^{2+} = 2.

enhanced and shifted to longer wavelengths (Figure). Mercuric ions at the same concentration also enhance, but do not shift, the circular dichroism bands. The Acridine Orange cation binds to the GMP polymer, and circular dichroism is induced in the absorption bands of the bound dye. The induced optical activity, as in the case of Acridine Orange bound to covalently-bonded helical polynucleotides[6] and polypeptides,[7] is due to a regular mutual orientation of the dye molecules bound to the polymer helix.

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