n-π* TRANSITIONS IN AZAPYRIMIDINE NUCLEOSIDES†

A.HOLY
Czechoslovak Academy of Science, Prague
G.T.ROGERS and T.L.V.ULBRICHT
Twyford Laboratories Ltd., Twyford Abbey Road, London, N.W.10, England

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Several years ago we noted that, whereas pyrimidine β-D-nucleosides give positive Cotton effects, the corresponding azapyrimidine nucleosides give negative ones [1, 2]. To investigate this further we extended our studies on azapyrimidine nucleosides and found that the ORD of $O^2,2'$-cycloazauridine (I) showed multiple Cotton effects, with obvious overlapping. We therefore embarked on C.D. studies in the hope of resolving these Cotton effects, and here present evidence that certain azapyrimidine nucleosides have a small long wave-length Cotton effect which is due to an n-π* transition. Subsequently we also observed n-π* transitions in pyrimidine nucleosides [3]; this is the first evidence of n-π* transitions in such compounds giving rise to Cotton effects.

The characteristics of n-π* transitions are:

1. low intensity of the U.V. absorption, which may be difficult to detect.
2. a blue shift on going from a non-polar to a polar solvent, with the biggest shift on going to water and a reduction in ϵ max.
3. in aqueous acid (nitrogen protonation) there is a further blue shift or the band may disappear altogether [4].

The C.D. spectrum of 6-azauridine (II) in water at pH 9 (anionic species) shows a small positive Cotton effect at 297 mμ, which does not correspond to any observed U.V. maximum (λ_{max}, 264 mμ; See fig. 1). There are also negative and positive Cotton effects at

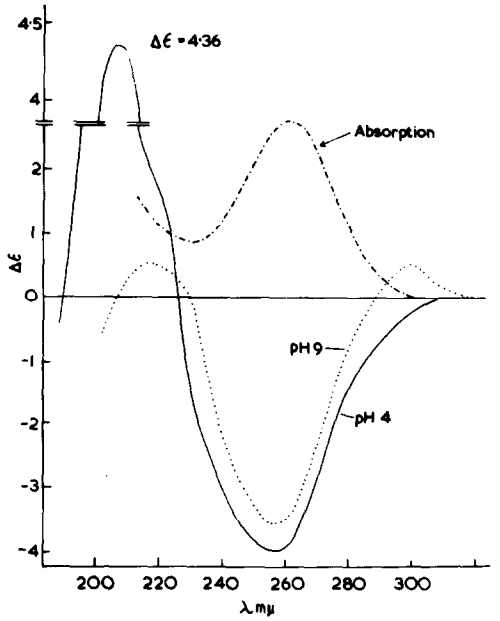
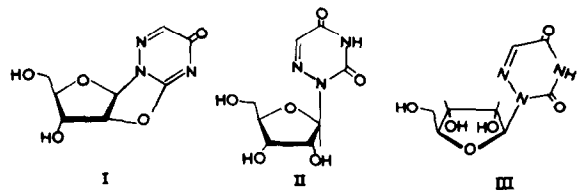


Fig. 1. U.V. Absorption and C.D. Spectra of 6-Azauridine (II).



Scheme 1.

† Optical Rotatory Studies of Nucleic Acid Derivatives, Part XII. Part XI, G.T.Rogers and T.L.V.Ulbricht, Biochem. Biophys. Res. Commun., in press.

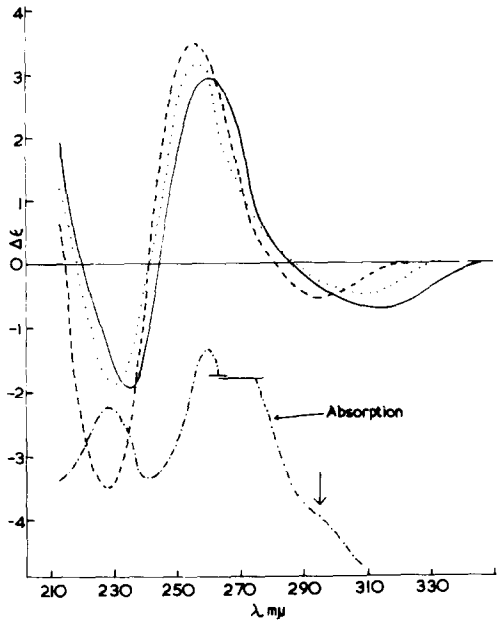


Fig. 2. U.V. Absorption (-.-.-.-) and C.D. Spectra (——) in Dioxan; (.....) in Acetonitrile; (- - -) in Water pH 7.0 of O^2 2′ Cycloazauridine (I).

259 and 215 mμ respectively. At pH 4 (protonated species) these latter Cotton effects are still found, but the Cotton effect at 297 mμ has disappeared (fig. 1). Almost identical results have been obtained with 5-methyl-6-azauridine (azathymine riboside).

L-6-Azauridine (III) gives similar results but, as expected, the Cotton effects are of opposite sign (at pH 9: neg. C.E. at 298, pos. C.E. at 260, neg. C.E. at 214 mμ. At pH 4, the C.E. at 298 vanishes).

Unfortunately 6-azauridine is too insoluble in non-polar solvents for studies to be carried out in them, but this was possible with O^2,2′-cycloazauridine (I). The C.D. spectrum of this compound in dioxan (fig. 2) shows several Cotton effects. The small Cotton effects at 312 mμ shows a small blue shift (3 mμ) on going to the more polar solvent acetonitrile, and a further, larger blue shift (15 mμ) on going to water. It is interesting that in the U.V. spectrum in water it is just possible to see a shoulder in the expected region (fig. 2, arrow).

These C.D. studies on four azapyrimidine nucleosides clearly indicate that the small Cotton effect in the 300 mμ region is due to an n-π^* transition.

References

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[2] T.R.Emerson, R.J.Swan and Tilo L.V.Ulbricht, Biochemistry 6 (1967) 843.
[3] See Following Paper.
[4] S.F.Mason, J. Chem. Soc. (1959) 1240, 1247.