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PHOTOCHEMICAL REACTIONS OF SOME PYRIMIDINE-PURINE DINUCLEOTIDES ANALOGS

S.Paszyc, B.Skalski and G.Wenska
Institute of Chemistry, A.Mickiewicz University, Poznań, Poland.

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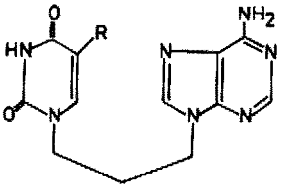
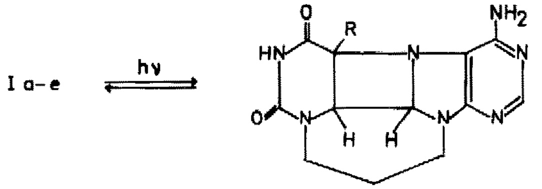


I a R= H
b R= CH_3
c R= C_2H_5
d R= n-C_3H_7
e R= n-C_4H_9

In this Laboratory we have become interested in the photochemistry of some dinucleotides analogs Ia,b,c,d,e, in which the sugar-phosphate group has been replaced by a trimethylene bridge /1/. These analogs were synthesized by direct alkylation of adenine with appropriate 1-/3-bromopropyl/-5-alkyluracils. This was accomplished in DMF solution in the presence of NaH. Irradiation of aqueous solutions of all analogs /c=10^{-4}M/l/ at 20°C /±1°/ during 15 min. with low pressure mercury lamp /253,7 nm/ leads to a photostationary state with a decrease of 20% in absorption coefficient at 263 nm. The TLC analysis of irradiated solutions of Ia,c,d,e revealed two photoproducts and only one for Ib, in addition to the starting materials. The main component of each mixture has been isolated and identified as an internal pyrimidine-purine photoadduct II. A significant decrease in absorption maximum in comparison to that of the substrates was observed together with a shift in λ_{max} towards longer wavelength: photoadducts IIa-e $\lambda_{max}^{H_2O}$ nm /ε/ ~285 /~6500/, analogs Ia-e $\lambda_{max}^{H_2O}$~263 /~19000/. This suggested the partial destruction of the pyrimidine residue and the adenine chromophoric system which has been also confirmed by characteristic differences in NMR spectra of Ia-e to those of IIa-e. In NMR spectra of IIa-e, in the absorption region expected for aromatic protons only one monoprotonic singlet is present at δ~7.75 which is assigned to the adenine C^2H. Hydrogen atoms at 5-alkyluracil C^6H and adenine C^8H are characterized by an AX system, thus in photoadduct spectrum two doublets at δ~5.70 and δ~4.30 /J_{AX}=4Hz/ are observed. Inspection of Dreiding's models showed that pyrimidine-purine linkage is only possible via a pyrimidine C^6 and purine C^8 bond, because of the trimethylene bridge length. Mass spectra of IIa-e are identical to MS of appropriate analogs. Photoadducts are thermally unstable and under experimental conditions /200°C/ the azacyclobutane ring is ruptured firstly.



IIabcde

Furthemore, reirradiation at 254 nm of aqueous solutions of photoadducts caused their partial decomposition, regeneration of starting material and the establishment of a photostationary state. Irradiation with wavelength longer than 290 nm causes almost complete regeneration of starting materials.

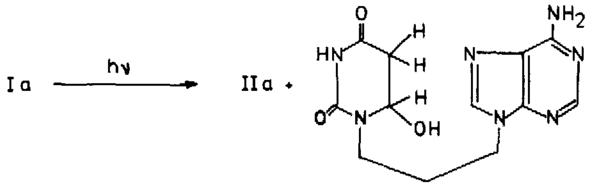
The above described physicochemical properties and together with NMR data of photoadducts suggest that the adducts have an aza-cyclobutane type adduct structure. The formation of II is one of the few examples of the double bond C=C to C=N photocycloaddition /2/.

A second photoproduct, identical for the three analogs /Ic,d,e/ was isolated from the irradiated mixture in about 3% yield. On the basis of NMR,UV and IR spectral data it was identified as the uracil-adenine analog /Ia/.

$$\mathrm{I\ c,d,e} \xrightarrow{h\nu} \mathrm{Ia} + \mathrm{R'CH{=}CH_2}$$

It formation is the result of photochemical dealkylation of 5-alkyluracil residues by a Norrish Type II Process /3/.

A third photoproduct has been isolated from the irradiated solution of Ia and assigned the photohydrate structure /III/ on the basis of analytical and spectral data, and of its acid-catalysed dehydration to Ia.



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