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EVIDENCE FOR SPIROCONJUGATION IN ANIONIC SIGMA COMPLEXES[1]

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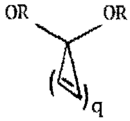
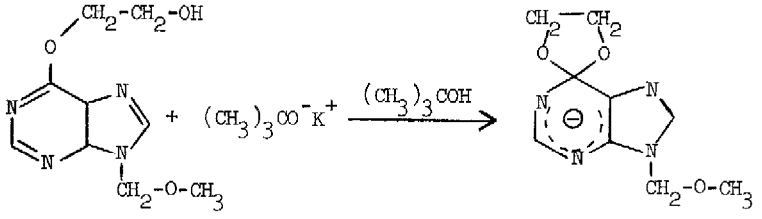
Spiroconjugation has been postulated to produce important and characteristic effects in the electronic spectra and in the chemical reactivity of certain classes of compounds containing four p centers located by D_2d symmetry on atoms bonded to a tetrahedral center[2-4]. Simmons and Fukunaga[2] have convincingly rationalized the electronic spectra of a large number of spiraenes (I) and cyclopolyene ketals (II) in terms of spiroconjugation as has Boschi, Drieding and Heilbronner[5] for the electronic spectrum of spiro[5.5]undeca-1,4,6,9-tetraene-3,8-dione. Semmelhack, *et. al.*,[6] have recently provided evidence which suggests that spiroaromaticity is not an important stabilizing factor in the 1,2-dimethyl-4-5,6-trichlorospiro[2.3]hexa-1,4-diene-6-yl anion. In this case, however, the presence of chlorine substituents could minimize spiroaromatic stabilization. In recent years, photoelectron spectroscopy has proven to be an extremely valuable tool for obtaining information concerning spiroconjugative interaction.[7-9] Using this technique excellent evidence for spiroconjugation has been presented for 9,9'-spirobifluorene, 9,9'-spirobi-(9-silafluorene), 1,1'-spirobiindene, spiro[4.4]nonatetraene and 1,4, 6,9, tetrathiaspiro[4.4]nonane.[10-14] We now wish to report the first evidence for spiroconjugation in anionic sigma complexes formed via an aromatic nucleophilic addition mechanism.

I



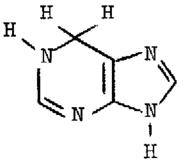
II

The reaction of 6-(β-hydroxyethoxy)-9-methoxymethylpurine (III) (5×10^{-5} M, λ_{max} 248 nm, τ=10,900) with potassium *t*-butoxide (0.07-0.28 M) in *t*-butyl alcohol produces new absorptions (λ_{max} 255 nm, τ=9,385 and λ_{max} 267,τ=7,700) attributed to anionic sigma complex IV. The NMR

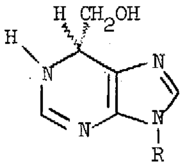


III IV

spectrum of the product of this reaction has been recently reported and is consistent with structure IV.[15] The u.v. spectra of 1,6-dihydropurine (V) and the diasteriomers of 1,6-dihydro-6-hydroxymethylpurine ribonucleoside (VI) have been reported. Both have a λ_{max} at 293 nm, τ=4,700 in water (pH = 7).[16-18] The u.v. spectrum of VI in t-butyl alcohol has been recently measured by Wolfenden and Evans (λ_{max} = 297.5 nm, τ=4,240) indicating only a slight



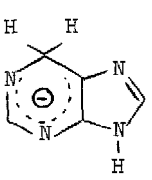
V



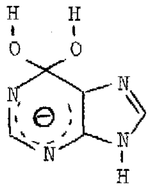
VI

R = ribonucleoside

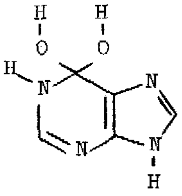
bathochromic shift in going from water to t-butyl alcohol.[19] The difference in λ_{max} between IV and the models V and VI is quite dramatic but not surprising since IV is capable of spiroconjugative interaction between the p orbitals on the ring and the p orbitals on the ketal oxygen atoms. This interaction would tend to destabilize the lowest unfilled π-molecular orbital on the ring causing the observed hypsochromic shift. In contrast, spiroconjugative interaction is not possible for models V and VI. The shift of 31 nm corresponds to an energy difference of approximately 10 kcal/mole. This is slightly larger than the energy differences found for the ketals of cyclopropenone and tropone (5-7 kcal/mole) when compared to the appropriate reference systems.[2] Extended Huckel calculations on systems VII, VIII and IX qualitatively reflect the experimental observations for the purine systems reported in this communication; an energy difference of 8.8 kcal/mole may be calculated for the electronic transition from the



VII



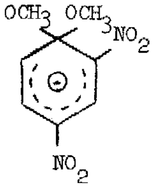
VIII



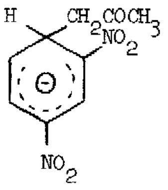
IX

highest filled to the lowest unfilled molecular orbitals in the comparison of VII to VIII and IX.[20] It is interesting to note that an enhancement of intensity of the heteropolyene band is observed for IV as compared to V and VI. A similar observation was reported for the ketals of cyclopropenone and tropone when compared to the appropriate reference models.[2]

The u.v. spectra of anionic sigma complexes X (λ_{max} 503 nm)[21] and XI (λ_{max} 536 nm)[22] in the solvent methanol again reveals the operation of spiroconjugation. This spectral shift corresponds to an energy difference of approximately 4 kcal/mole.



X



XI

Spiroconjugation is probably a general phenomenon for anionic sigma complexes having two p orbital containing atoms bonded to the tetrahedral center. Unfortunately, the comparison between the spiroconjugated and reference systems is difficult, since the electronic spectra reported in the literature are usually determined in different solvents. In addition, since the vast majority of anionic sigma complexes are polynitro-containing systems, a possible change in conformation of a proximate nitro group with changes in substitution at the tetrahedral center makes interpretation of the magnitude of the spectral shifts somewhat tenuous. This, of course, is not a problem with the purine system.

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