storage (the Ayer samples we obtained had been stored for more than 20 years).

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Generation and Characterization of 2,6-Azulylene

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Polyenic molecules continue to be important in providing a basis for the discovery of the fundamental features of molecular electronic structures.¹ 2,6-Azulylene (1) contains the potential for probing for many electron effects in a nonalternant² π system. We wish to report a short synthesis of the [2.2]2,6-azulenophane mixture^{3,4} 5 which allowed us a clean method to generate 1 and hence to determine some of the spectral and chemical properties of this reactive polyene.

The synthesis of the cyclophane mixture 5, in the same syn and anti regioisomer ratio as obtained before,^{3,4} is shown in Scheme I. A tetrahydrofuran (THF) solution of sodium cyclopentadienide was treated with 1 equiv of diethyl carbonate, followed by nbutyl-4-picolinium bromide (1.0 equiv), giving a 1:1 mixture of 1- and 2-carboethoxy-6-methylazulenes (2). Addition of this mixture to an equivalent of sodium hydroxide in aqueous ethanol caused the highly selective hydrolysis of the isomer bearing the carboethoxy group in the 2-position. After neutralization, 2carboxy-6-methylazulene was isolated in 9.3% overall yield from cyclopentadiene. This application of the Hafner⁵ azulene synthesis can easily provide the carboxylic acid precursor to the target [2.2](2,6)-azulenophane mixture 5 in gram quantities in 2 days. The acid produced here is isomeric with that used by Keehn³ in preparation of 5 and the remainder of our synthesis (Scheme I) is similar to his procedure. The Hofmann elimination, from the present quaternary ammonium hydroxide 4, proceeded at 85 °C in toluene/ H_2O and gave the cyclophane mixture (5, syn and anti) in 11% yield. The composition of this mixture (anti-5:syn-5 = 2:3 by 360-MHz ¹H NMR: δ 7.61, doublet, H_{4,8} anti isomer; δ 7.66, doublet, H_{4,8} syn isomer) was nearly the same as that observed by Ito.4

Figure 1 shows the proton magnetic resonance (¹H NMR, 360 MHz) spectrum of an acetone- d_6 solution of material obtained by passage of 5 through our⁶ flash vacuum pyrolysis (FVP) device at 620 °C after collection and transfer below 170 K. The ¹H NMR spectrum confirms that dissociation of 5 is clean as expected from previous reports.7

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Figure 1. 360-MHz proton magnetic resonance spectrum of 2,6-azulylene (1); acetone- d_6 , -80 °C. Tentative assignments based on CNDO/S carbon atom charge densities.

Scheme I



Figure 2 shows the optical absorption, fluorescence, and partial excitation spectra of solutions of the FVP condensate from 5. The absorption bands between 300 and 420 nm all disappeared at room temperature by phenomenological second-order kinetics.8 Second-order rates of disappearance of 1 are expected if the polymerization process is self-initiated. Chloroform extraction of the polymeric main product, formed from 1 on warming, yielded a cyclophane mixture 5 of the same composition (syn:anti = 3:2)

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Figure 2. Absorption, fluorescence, and excitation (426-nm emission) of 3-methylpentane solutions of 1 at low (<-80 °C) temperature. HAM3/CI and CNDO/S estimates of the vertical excitation energies are shown by bars at the top $({}^{1}A_{1}^{**}$ designates excitation state with a large contribution from electron pair (two electron) promotion).

as from the Hofmann elimination (Scheme I), supporting the notion that 1 is indeed an intermediate in the formation of 5 under those conditions.



The fluorescence spectrum shown in Figure 2 was obtained after subtraction of contributions from fluorescent impurities and the products of reaction of 1. The emitting species, responsible for this part of Figure 2, was found to disappear with an apparent second-order rate constant that was approximately the same as the value (relative) found for the absorbing species (1). This observation suggests that the fluorescence depicted in Figure 2 is also due to 1. If that is the case then it suggests at least two excited states in the 300-420-nm absorption region with emission from the higher one. 2,6-Azulylene (1) would then be another example of a system exhibiting (anti-Kasha)9 fluorescence from a higher than first excited state (at least in part). The preliminary¹⁰ excitation spectrum (Figure 2) supports this rationalization.

The Raman (457.9-nm excitation) spectrum of THF solution (-40 °C) of the FVP condensate of 5 shows five clear maxima in the C-C valence stretching region (1600, 1514, 1480, 1463, and 1446 cm⁻¹) after corrections for solvent and reaction product

(10) The high reactivity of 1 complicates the interpretation of the excitation spectra. The most significant observation is the disappearance of excitation of the strong 404- and 425-nm emission lines at excitation wavelengths greater than 380 nm.

background. This spectrum also supports the assignment of the FVP products structure as 1. Five resonance enhanced fundamentals are expected if the lowest (410-nm onset, Figure 2) transition is ${}^{1}B_{2}$. However, additional spectra at varying excitation frequencies would be required before such an assignment could be considered secure.

Figure 2 shows the predictions of the vertical excitation energies of the first several singlet excited states of 1 using CNDO/S¹¹ and HAM3/CI12 models. Both models agree that at least two (essentially) single electron excitation states $({}^{1}A_{1}, {}^{1}B_{2})$, and one state containing a significant population of a two-electron excitation $({}^{1}A_{1}^{**})$ should be located in the 300-510-nm region of the spectrum. The CNDO/S calculations^{11a} are in reasonably good accord with the superficial absorption band shape. The HAM/3 procedure appears to underestimate the HOMO-LUMO gap to a considerable extent.

In summary, we believe we have provided an efficient way to obtain 1. The stability of this reactive polyene is sufficient to allow good spectroscopic characterization. The CNDO/S calculations suggest that the ordering of the first two of its one-electronpromoted states is ${}^{1}B_{2}$ lower than ${}^{1}A_{1}$.¹³ We hope to be able to examine the spectral properties of 1 in greater detail, especially its photoelectron spectrum which may reveal, in an unambiguous manner, the many electron effects predicted by the non-Koopmans¹⁴ model.

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Hydrophobic Perturbation of Acyclic Equilibria

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Many enzymatic processes occur at interfaces between aqueous and hydrophibic media. Stereoselectivity in many of these conversions has been attributed to hydrophobic forces that favor the formation of one stereoisomeric form.^{1,2} While there has been a considerable effort expended to understand the nature of the hydrophobic effect in biological systems such as lipid bilayer membranes, studies directed at revealing the influence of amphiphilic aggregates such as micelles and bilayers on organic stereochemistry are relatively rare.³⁻⁵ We have recently reported that molecular aggregates dramatically influence the stereo-

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