Purification and Electronic Spectroscopy of Polyenes
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Polyenes are $\pi$-conjugated systems with alternating double and single C-C bonds that play important photochemical and photobiological roles such as photoprotection and photosynthesis enhancement in plants and photosynthetic bacteria. The excited state energies and photochemical properties of polyenes depend on the number of conjugated double bonds ($N$). Theoretical calculations have suggested that the energies of the excited electronic states of polyenes and carotenoids approach a common limit as $N\to \infty$. We have obtained absorption spectra of the allowed electronic energy transitions for synthetic polyenes with $N=5$-$23$. These transitions appear to approach a common long-polyene limit, and we have compared our experimental results with the predictions of simple Hückel theory and the particle-in-a-box model, using parameters to account for the effects of bond alternation in these systems. For longer polyenes ($N \geq 4$), the first allowed electronic transition (HOMO $\to$ LUMO) does not represent the lowest excited singlet state. The lowest excited singlet state ($S_1$) is symmetry-forbidden, and the $S_1$ state determines many of the photochemical properties of polyenes and thus is the most interesting and important energy state to understand. Low-temperature (77 K) fluorescence spectroscopy was used to estimate the $S_1$ energies in polyenes with $N=5$ and $N=7$. The $S_1\to S_0$ fluorescence yields of these molecules decrease with $N$, thus making it more difficult to obtain resolved fluorescence spectra for $N > 7$.

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