Rotationally Resolved Electronic Spectra of *trans,trans*-Octatetraene and Its Derivatives

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Described herein are the rotationally resolved one-photon fluorescence excitation spectra of several vibronic bands in the $S_1 \leftarrow S_0$ electronic transitions of three linear polyenes in the gas phase, 1,3,5,7-octatetraene (OT), 1,3,5,7-nonatetraene (NT), and 2,4,6,8-decatetraene (DT). Several of the spectra are significantly perturbed by an apparent centrifugal distortion in the S_1 state of OT, owing to the high frequency of rotations parallel to *a* and the low frequency of an in-plane bending mode (ν_{48}), by Coriolis coupling in the S_1 state of NT, involving ν_{48} and a nearby methyl torsional level, and by torsion–rotation coupling in the S_1 states of NT and DT, owing to a significant reduction in the excited-state torsional barrier(s) compared to the ground state. Nonetheless, the inertial parameters of eight different S_0 and S_1 vibronic levels have been determined, from which it is concluded that the carriers of the spectra are in all cases the *trans,trans* isomers. The important role of ν_{48} as a promoting mode for S_1–S_2 vibronic coupling, the source of the $S_1 \leftarrow S_0$ oscillator strength, is confirmed. Finally, the measured differences in the rotational constants of the S_0 and S_1 states (e.g., $\Delta A = 2532$, $\Delta B = -11.7$, and $\Delta C = -11.0$ MHz for the vibronic origin of OT) provide new information about the changes in geometry that occur when the photon is absorbed.

Introduction

Polyenes (C_nH_{n+2}), molecules with alternating single and double bonds between covalently attached carbon atoms, are an important class of molecules with many interesting properties.[1] Among these is geometrical isomerism, by far the most significant property of polyenes in biological systems. Each 180° turn at either a single or a double bond gives a different configuration, resulting in a large number of possible structures, especially when *n* is large. Thus, octatetraene ($n = 8$) has 20 distinguishable isomers, although three or four consecutive *cis* configurations result in steric crowding that may prevent their formation. The net count in C_8H_{10} is 15, excluding *cis*[3] configurations, and 18, excluding *cis*[4] configurations.[2]

Given this fact, the existence of a controversy concerning the correct assignment of the electronic spectrum of octatetraene is not surprising. Heimbrook et al.[3] observed $S_2 \rightarrow S_0$ ($1^1B_u \rightarrow 1^1A_g$) emission from the gas-phase molecule and recorded its strongly allowed $S_2 \leftarrow S_0$ fluorescence excitation spectrum. However, they were not able to detect the dipole forbidden $S_1 \leftrightarrow S_0$ ($2^1A_g \leftrightarrow 1^1A_g$) transition under isolated molecule conditions. Later, Buma et al.[4] obtained the two-color REMPI spectrum of the 2^1A_g state in the gas phase and assigned their spectrum to a "*cis, trans*" isomer. They argued that only a noncentrosymmetric isomer would have a large enough oscillator strength to be detected under their experimental conditions. Then, Petek et al.[5] succeeded in observing the $S_1 \rightarrow S_0$ fluorescence of octatetraene in a supersonic jet and recording

its one- and two-photon $S_1 \leftarrow S_0$ fluorescence excitation spectra. A detailed comparison of these spectra led to the conclusion that the carrier is the *trans,trans* isomer, the most stable form. This conclusion was supported by a more recent study of the fluorescence excitation spectra of two additional "linear" tetraenes, nontetraene and decatetraene, in which one or both terminal hydrogen atoms in octatetraene are replaced by methyl groups.[6,7]

Rotationally resolved electronic spectroscopy is a powerful method for establishing the identity of gas-phase chromophores. The patterns of energy levels observed in this experiment are sensitive both to the size and shape of the molecule and to how these change when a photon is absorbed.[8] Here, we demonstrate the utility of this approach in a study of the high-resolution one-photon fluorescence excitation spectra of octatetraene, nonatetraene, and decatetraene in the collision-free environment of a molecular beam. The results provide an unambiguous identification of the isomers responsible for the above-mentioned spectra as the *trans,trans* forms. The spectra also give new insight into the remarkable photochemical and photophysical properties of the polyenes and provide new experimental benchmarks for evaluating theoretical descriptions of their 2^1A_g states.

Experimental Section

Octatetraene (OT) was prepared by dehydrating 1,4,6-octatrien-3-ol at 80 °C using pyridinium *p*-toluenesulfonate (Aldrich) following the procedure developed by Yoshida and Tasumi.[9] The 1,4-octatrien-3-ol was produced by mixing 2,4-hexadienal with vinylmagnesium bromide (Alfa). The dehydra-

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tion produces *trans*,*trans*-OT of >99% isomeric purity as determined by an analysis of the $S_2 \leftarrow S_0$ spectrum in a free jet.[5] The OT crystals were stored at -80 °C to preserve their isomeric purity. Nonatetraene (NT) and decatetraene (DT) were synthesized from Wittig reactions, using hexadienal and allyltriphenylphosphonium bromide (Fluka) for the former and hexadienal and crotyltriphenylphosphonium bromide (Fluka) for the latter.

Supersonic jet spectra were obtained using a standard low-resolution apparatus. Typically, the polyenes (OT at room temperature, NT and DT with mild heating) were seeded into 80 psig He and expanded through a pulsed 1 mm nozzle (General Valve, series 9). The resulting free jet was crossed with a frequency-doubled Quanta-Ray Nd^{3+}:YAG-pumped dye laser beam about 1 cm downstream of the nozzle. When tuned to a particular vibronic band in the absorption spectrum, the laser produced $S_1 \rightarrow S_0$ fluorescence, which was collected by a single lens system, detected by a photomultiplier tube and SRS

The excited-state parameters of the two bands listed in Table 2 were determined separately by fixing the S_0 rotational constants at the experimental values shown in Table 1 and varying the S_1 rotational constants to obtain least-squares fits. These calculations showed that both excited-state vibrational levels are nonrigid, requiring the full Watson Hamiltonian[14] for their analysis. For the band at $0_0^0 + 76.2$ cm^{-1} (band OT-1), we fit 353 transitions with a standard deviation of 11.0 MHz. For the band at $0_0^0 + 411.9$ cm^{-1} (band OT-2), we fit 192

exhibits the same large, monotonic shifts of its K_a subbands that were observed in bands OT-1 and OT-2 of *trans*

subband with $K_a \geq 1$ is split into two components, with the center of gravity of the two components shifting to the red with increasing K_a. Qualitatively similar behavior is exhibited by the K_a subbands in the rotationally resolved spectrum of the

now spread over three torsional levels having different nuclear

However, only the *trans,trans* form (**I**) has calculated B'' and C'' rotational constants that agree with those measured in this work. For NT, the best agreement between experiment and theory also is obtained for the *trans,trans* isomer. Here, we find from our fit of band NT-2 the values $A'' = 16\ 102 \pm 2.3$, $B'' = 390.2 \pm 0.1$, and $C'' = 382.1 \pm 0.1$ MHz, whereas theory (CASSCF)[16] gives the values $A'' = 16\ 090$, $B'' = 390.0$, and $C'' = 381.9$ MHz. Thus, we confirm the conclusions of Petek et al.[5−7] The carriers observed in their spectra of OT, NT, and DT are primarily the *trans,trans* forms. These data also show that modern ab initio theory gives an accurate description of the structures of the isolated molecules in their ground electronic states.

occupied $\pi^*_{C=C}$

It is interesting to note that the CASSCF geometry of the 1^1B_u state of *trans,trans*-OT has rotational constants of $A = 20\,148$, $B = 559$, and $C = 544$ MHz.[16,18] The calculated values of B and C for the 1^1B_u state are nearly the same as those for the 2^1A_g state. However, the calculated value of A for the 1^1B_u state is significantly larger than the corresponding value for the 2^1A_g state. Thus, if the degree of mixing of the two states via the b_u promoting mode is large, this may account for at least some of the discrepancy between the observed and calculated values of ΔA for the 2^1A_g state.

Making such arguments quantitative is a challenging task.[34] In early work, Kohler and co-workers[35−37] invoked vibronic coupling between the ground 1^1A_g and excited 2^1A_g states to explain the increase in frequency of the Franck−Condon active, totally symmetric C=C stretch that was observed on excitation of 2,10-dimethylundecapentaene and 2,12-dimethyltrideca-hexaene. Later, Orlandi and Zerbetto[38] showed that, whereas vibronic couplings between states of the same parity are strong and are caused predominantly by C−C stretching modes, the couplings between states of opposite parity are comparatively weak and involve mainly C−C−C bending modes. More recently, Buma and Zerbetto[39] used CI methods to investigate vibronic intensity patterns in the spectrum of *trans,trans*-OT. They found that the low-frequency b_u mode (ν_{48}) is most active in coupling the two ^1A_g and $1\ ^1B_u$ states. They also confirmed that the intensity of the false origin in the one-photon excitation spectrum of *trans,trans*-OT is comparable to that of the true origin in an OT containing a *cis* linkage, as previously discussed by Petek et al.[5] Future modeling of this effect should focus on *trans,trans*-NT, in which both the true and false origins are observed (cf., Figure 1). Quantitative estimates of the vibronic coupling matrix elements are needed to account for the large variations in time scales that have been observed in the excited-state relaxation behavior of several polyenes.[40]

Conclusions

Rotationally resolved electronic spectra of several vibronic bands in the $S_1 \leftarrow S_0$

+3 MHz from the HF/6-31G* calculations (ref 18). Thus, ΔA, although having the right order of magnitude, has the wrong sign to explain this discrepancy.

(23) Negative ΔA values have been found in DPB (ref 12) and tS (ref 13), but in these cases the observed changes appear to be associated primarily with increases in the lengths of the C−C bonds in the phenyl rings that are most perpendicular to a.

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