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Resonance Raman and Absorption Spectroscopy of the Lowest Triplet State of 1,3,5-Hexatriene and Deuteriated Derivatives at 183 K: Molecular Structure in the $T_1$ State

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Time-resolved resonance Raman (RR) spectra of the lowest excited triplet state $T_1$ of (E)-1,3,5-hexatriene, (E)-3-deuterio-1,3,5-hexatriene, and (E)-1,1-dideuterio-1,3,5-hexatriene are obtained at 183 K. The $T_1$ potential energy surface (PES), determining energy minima, equilibrium geometries, frequencies, and normal modes of vibration, is calculated, and RR intensities are obtained on the basis of the Franck-Condon mechanism. By comparison with the calculated spectra, the observed RR spectra are assigned to an equilibrium mixture of planar $E$ and $Z$ species in the $T_1$ state. The relative intensity of the $E$ and $Z$ bands at temperatures between 293 and 183 K gives an upper limit of 0.22 kcal/mol for the energy difference between the planar $E$ and $Z$ forms. Time-resolved triplet-triplet absorption measurements as a function of temperature between 296 and 183 K yield a frequency factor $A$ of $1.6 \times 10^4$ s$^{-1}$ and an apparent activation energy $E_a$ of 0.7 kcal/mol for the decay of the $T_1$ state. Consequently, an upper limit of 0.7 kcal/mol above the planar $E$ and $Z$ geometries is established for the possible local energy minimum at the twisted geometry. On the basis of these data, a PES is proposed for the $T_1$ state of 1,3,5-hexatriene with respect to torsion around the central CC bond and the $C_2C_3$ and $C_4C_5$ bonds.

I. Introduction

1,3,5-Hexatriene is an important model in studies of the photochemistry and photophysics of polyenes. The sensitized photoisomerization of 1,3,5-hexatriene (HT) proceeds through the lowest excited triplet state $T_1$. In a recent paper we compared the $T_1$ resonance Raman (RR) spectra of (E)-1,3,5-hexatriene (EHT) and (Z)-1,3,5-hexatriene (ZHT), and in another one we discussed quantum chemical calculations of $T_1$ absorption and RR spectra and compared the theoretical results with experimental $T_1$ RR spectra from deuteriated hexatrienes: EHT, (E)-3,4-dideuterio-1,3,5-hexatriene ((E)-HT-3,4-d$_2$), and (E)-2,5-dideuterio-1,3,5-hexatriene ((E)-HT-2,5-d$_2$). We have also investigated various methylated derivatives of HT (ref 3, and references therein). All measurements were performed at room temperature in solution.

We found that the $T_1$ RR spectra of EHT and ZHT were identical, which we interpreted in terms of equilibration along the torsional coordinate of the central CC bond on the $T_1$ potential energy surface (PES) during the lifetime of $T_1$. Furthermore, from the comparison of experimental and theoretical results, we concluded that for HT two relative minima at planar $E$ and $Z$ geometries on the $T_1$ PES exist, and that both forms contribute to the RR spectrum, the $E$ form being predominant and hence of lowest energy. While no evidence was found of the presence of a perpendicular form, twisted by 90° at the central CC bond, a substantial population of this form could not be excluded.

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In the present paper, the study of $T_1$ HT is further pursued in two ways: (i) by recording of $T_1$ RR spectra at lower temperature and (ii) by investigation of additional deuteriated derivatives.

Several effects of lowering the temperature can be envisaged: (i) As the temperature is lowered, and the viscosity of the solution increases, diffusion processes, such as triplet energy transfer from the sensitizer to HT, and from HT to possible impurities, will be slowed down, thus influencing the kinetics of the buildup and possibly the decay of $T_1$. (ii) With increasing viscosity, friction may become more important for the dynamics of the species in the $T_1$ state. (iii) The temperature will affect the rates of interconversion between the species corresponding to different minima on the $T_1$ PES and may influence the relative populations. When equilibration along the torsional coordinate is no longer possible, different spectra will be observed from solutions containing either the $E$ or the $Z$ ground-state isomer. If equilibration prevails, changes in the populations of the species present will be reflected in their contribution to the observed spectra. (iv) A narrowing of the population distributions at low temperature is expected to give rise to narrower Raman lines, improving resolution.
Lowest Triplet State of 1,3,5-Hexatriene


and sensitivity. (v) The lifetime of the triplet species, which may be affected by temperature in different ways, is observable from time-resolved RR or optical absorption measurements.

Investigation of additional deuteriated derivatives of (E)-1,3,5-hexatriene may provide a further test for the correlation between observed and calculated T1 RR spectra. In particular, asymmetrical deuterium substitution increases the number of symmetry-allowed Raman bands of T1, 1,3,5-hexatriene. We have recently published a study of the Raman and infrared spectra of ground-state EHT, (E)-HT-3,4-d2, (E)-3-deuterio-1,3,5-hexatriene ((E)-HT-3-d), (E)-1,1-dideuterio-1,3,5-hexatriene ((E)-HT-1,1-d2), and (E)-HT-2,5-d2, in order to improve the force field of (E)-1,3,5-hexatriene in the ground state.4

In the present paper, we report the time-resolved RR spectra of the lowest triplet state T1 of EHT, ZHT, (E)-HT-3-d, and (E)-HT-1,1-d2, obtained in solution at 183 K. Using a modified version of the semiempirical quantum mechanical consistent force field program (QCCF/ps),4,5 calculations are performed on the T1 state of the deuteriated compounds in the planar E, planar Z, and perpendicular or twisted (Tw) geometries. The structure of the T1 state of 1,3,5-hexatriene is discussed by comparison of the experimental and theoretical results. In addition, we report time-resolved UV absorption measurements of the T1 state of EHT as a function of temperature (296–183 K).

II. Experimental Methods

A. Materials. Acetonitrile-d3 (Fluka, puriss., >99.8% D), cyclopentane (Fluka, for UV spectroscopy), methanol (Merck, p.a.), and acetone (Merck, p.a.) were used as received. 1,3,5-Hexatriene was obtained from Aldrich as a mixture of the E and Z isomers. The separation of the isomers has been described in detail previously.6 The synthesis of (E)-HT-3-d and (E)-HT-1,1-d2 has been described before.4 Capillary gas chromatography (BP1 or DB225 columns, 50 °C. He carrier gas) showed (E)-1,3,5-hexatriene to be 99.4% pure (0.6% (Z)-1,3,5-hexatriene), (Z)-1,3,5-hexatriene 99.3% pure, (E)-HT-3-d 98% pure, and (E)-HT-1,1-d2 96% pure.1H NMR spectrometry (Bruker WM250, 250 MHz) of the deuteriated products indicated a high deuterium content (>95%).

The purified samples were distilled into glass capillaries under reduced pressure. The capillaries were cooled briefly, sealed, and kept in a freezer. Throughout the experiments, the capillaries with trienes were opened and solutions prepared and transferred to sample cells under an Ar atmosphere. Prior to the addition of triene, the solvents were purged with Ar for more than 35 min.

B. Raman Measurements. The experimental procedures for the time-resolved RR experiments have been described previously.1,3 The triplet state of 1,3,5-hexatriene was produced by exciting acetone as sensitizer with a pump pulse (308 nm, ca. 5 mJ per pulse at the sample) from an excimer laser (Lambda Physics EMG 102E). The RR spectrum of 1,3,5-hexatriene in the T1 state was obtained by using the second harmonic from a Nd:YAG-pumped dye laser (Quantel) as probe pulse (315 nm, ca. 2 mJ per pulse at the sample). Both lasers were pulsed at 5 Hz with pulse lengths of 10–15 ns, pump–probe time delays ranging from 60 to 1080 ns.

The detection system has been described in detail before.3 Scattered Raman light was dispersed in a single-grating spectrometer (f = 600 mm, 2400 grooves/mm). The TV-based detector described previously has been replaced with a gated (30 ns) intensified photodiode array (OSMA IR4-700 from Spectroscopy Instruments) with 700 active channels. A polarization scrambler was placed in front of the spectrometer.

We constructed a new sample cell holder for time-resolved RR spectroscopy at low temperature. The sample was contained in a cylindrical Suprasil cell with 26-mm inner diameter and 6-mm inner height. This cell was placed in a spinning copper block, which was cooled by dry N2 gas and contained in an insulating housing with a top window for the incoming laser light and a side window for the scattered Raman light. The N2 gas was supplied by leading it through a copper spiral immersed in a liquid N2 Dewar vessel. The temperature was monitored with a Chromel–Alumel thermocouple or a Pt-100 resistance sensor placed close to the copper block and was regulated by varying the flow of the N2 gas. The top and side windows of the housing were flushed from outside with dry N2 gas to keep away dew. After a predefined temperature was reached in the copper block, the cell was allowed to equilibrate for at least 20 min to reach thermal equilibrium. The temperature of the cell was kept at 183 K for cyclopentane and methanol as solvents, and at 237 K when acetonitrile-d3 was used.

The chemical composition of the solutions was monitored by gas chromatography (GC; for conditions, see above) before the laser experiments to ensure purity, and after the experiments to follow isomeric conversion during the laser flash photolysis. The conversion between isomers was also followed by evaluating the resonance Raman spectra of the solutions with respect to vibrational bands from the ground states of different hexatriene isomers.

C. Absorption Measurements. In the time-resolved UV absorption measurements, the sample was irradiated with a pulse from the excimer laser at 308 nm, with a pulse energy of ca. 10 mJ at the sample. The triplet–triplet absorption was measured at right angles to the laser beam with a pulsed Xe lamp, a single-grating monochromator (Jobin Yvon H-20, f = 200 mm) placed after the cell, and a photomultiplier (Hamamatsu 955) coupled to a digital storage oscilloscope (LeCroy 9400). The analyzing wavelength was 318 nm, the spectral bandpass was 8 nm. The absorbance (from sensorizer) at 308 nm was ca. 1 per cm. The laser beam was focused to an area of 2 × 20 mm. The path length of the analyzing light was 20 mm, and the light was masked at the cell to an area of 2 × 4 mm.

The sample was contained in a cylindrical cell with a volume of 5 mL. This cell was placed in a copper block, which was cooled by cold, dry N2 gas and contained in an insulating housing. The temperature was monitored with a Pt-100 resistance sensor placed in the copper block and was regulated by varying the flow of the N2 gas. After a predefined temperature in the copper block was reached, the cell was allowed to equilibrate for at least 20 min. Again, the chemical composition of the solution was monitored by GC before and after the experiments. Whereas each Raman spectrum was averaged over many laser pulses, the time-resolved absorption data were obtained with single pulses.

III. Experimental Results

Raman experiments are reported for the following argon-saturated solutions: (1) cyclopentane, 0.817 M acetone, 0.015 M EHT; (2) cyclopentane, 0.817 M acetone, 0.018 M ZHT; (3) methanol, 0.817 M acetone, 0.012 M EHT; (4) cyclopentane, 0.408 M acetone, 0.011 M (E)-HT-3-d; (5) acetonitrile-d3, 0.545 M acetone, 0.005 M (E)-HT-3-d; (6) cyclopentane, 0.408 M acetone, 0.009 M (E)-HT-1,1-d2; (7) acetonitrile-d3, 0.545 M acetone, 0.009 M (E)-HT-1,1-d2. In the time-resolved absorption measurements the solution was (8) methanol, 0.408 M acetone, and 0.018 M EHT.

Subtraction techniques used in the Raman spectra have been discussed in detail previously.1 Each sample cell was used to obtain spectra by use of (a) the probe laser only, (b) both pump and probe lasers at 60–80 ns time delay between the pump and probe laser pulses, (c) both pump and probe lasers at longer time delay (500–1080 ns), and (d) two probe lasers. Tongue spectra were obtained from spectra b after the subtraction of spectra a and c. Subtraction of spectra a from spectra d allowed the identification of Raman bands arising from stable products of isomerization. The isomeric conversion was also monitored by GC. For 0.012 M EHT in methanol (solution 3), the amount of Z isomer grew from 0.6% to 12% during the experiments. For (E)-HT-3-d, the amount of Z isomer grew from 2% to 10% for the experiments

at 560-11s delay, with appropriate scaling factors. S denotes methanol and D-F one ground-state isomer to the other are shown in Figure 1.

Subtraction of spectra of type a from spectra of type d is shown in Figure 1A for (E)-HT-3-d (solution 8), the amount of Z isomer grew from 0.6% to 2.1% during the experiments. For (E)-HT-1,1-d2, the amount of Z isomer grew from 4% to 12% during the experiments with 0.009 M (E)-HT-1,1-d2 and 0.545 M acetone in Ar-saturated acetonitrile-d, solution at 293 K after 1200 pump-and-probe pulses. (B) (E)-HT-1,1-d2 in cyclopentane (solution 7). Similar subtraction spectra are found in ref 2 for (E)-HT-3,4-d2 and (E)-HT-2,5-d2. The negative bands represent depletion of ground-state E isomer, and the positive bands creation of ground-state Z isomer, during the laser flash photolysis experiments. As the spectra of the Z isomers have not been observed before, we list in Table I the frequencies of the strong preresonance Raman bands of ground-state (E)-HT-3,4-d2, (Z)-HT-3,4-d2, (E)-HT-3-d, (Z)-HT-3-d, (E)-HT-1,1-d2, (Z)-HT-1,1-d2, (E)-HT-2,5-d2, and (Z)-HT-2,5-d2. In addition, the spectra in Figure 1 show where one may expect artifacts in the transient triplet spectra reported below, due to changes in the ground-state population of the E and Z isomers. As shown previously,1 the E and Z isomers of 1,3,5-hexatriene yield identical triplet spectra, but the ground-state spectra are different for the two isomers, as seen from Figure 1 and Table I together with previously published spectra.2,3,4

B. Comparison of $T_1$ RR Spectra of EHT and ZHT at 293 and 183 K. Comparison of spectra obtained at different temperatures is shown in Figures 2 and 3, in order to illustrate the effect of lowering the temperature. Figure 2A shows a probe-only, type a, spectrum of EHT in methanol (solution 3) at 183 K. Figure 2B a pump-and-probe, type b, spectrum at 80-ns delay, and Figure 2C a pump-and-probe, type b, spectrum after subtraction of spectra of types a and c. Parts D-F of Figure 2 show corresponding spectra obtained in methanol at 293 K. The high wavenumber region of spectra 2C and 2F, after rescaling of 2F, is shown in Figure 3. Spectrum 2A (2D) shows ground-state bands from solvent, acetone, and EHT. In spectrum 2B (2E) additional, transient bands appear due to creation of the excited triplet state by the pump laser; the overall intensity is decreased by a factor of 2 due to transient triplet absorption. In spectra 2C (2F) and 3A (3B) the transient triplet bands are seen alone, after subtraction of ground-state bands from solvent and EHT.

The ground-state probe-only spectrum is stronger at 183 K (2A) than at 293 K (2D), in part due to a decrease in bandwidth at lower temperature. The same effect is seen in the pump-and-probe spectrum (2B, 2E), but much more pronounced is the increase at 183 K (2B) in the relative intensity of the additional, transient bands. This effect is found again in the subtraction spectrum of the triplet state (2C, 2F, 3A, 3B) and is reflected in the better signal-to-noise ratio of spectrum 3A compared to 3B. Besides the signal-to-noise ratio and the bandwidths, no significant dif-

Figure 1. (A) Difference preresonance Raman spectrum excited at 315 nm of 0.011 M (E)-HT-3-d and 0.408 M acetone in Ar-saturated cyclopentane solution at 183 K after 1200 pump-and-probe pulses. (B) Difference preresonance Raman spectrum excited at 315.75 nm of 0.009 M (E)-HT-1,1-d2 and 0.545 M acetone in Ar-saturated acetonitrile-d, solution at 293 K after 400 pump-and-probe pulses.

Figure 2. Raman spectra of Ar-saturated solution of 0.012 M EHT in methanol containing 0.817 M acetone. Spectra A–C obtained at 183 K, spectra D–F at 293 K. Spectra A and D, with the probe pulse only; B at a delay of 80 ns and E at a delay of 60 ns between pump-and-probe pulses; C, subtraction from B of A and pump-and-probe spectrum at 1080-ns delay, with appropriate scaling factors; F, subtraction from E of D and pump-and-probe spectrum at 560-ns delay, with appropriate scaling factors. S denotes methanol and X acetone. Pump wavelength 308 nm, probe wavelength 315 nm. Relative scales A–F: 1, 2, 2, 1, 2, 2; all spectra in the region 1000–100 cm$^{-1}$ are scaled up 4 times relative to the spectra in the region 1800–600 cm$^{-1}$. 


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TABLE I: Frequencies (cm\(^{-1}\)) of Raman Bands of Ground-State (E)-HT-3,4-d\(_d\), (Z)-HT-3,4-d\(_d\), (E)-HT-3-d, (Z)-HT-3-d, (E)-HT-1,1-d\(_d\), (Z)-HT-1,1-d\(_d\), (E)-HT-2,5-d\(_d\), and (Z)-HT-2,5-d\(_d\).

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*Excitation wavelength, solvent, and temperature are listed. *Reference 2.

In order to compare the \(T_1\) RR spectra of EHT and ZHT at low temperature, we recorded the transient triplet spectra of EHT and ZHT in cyclopentane (solutions 1 and 2) in the region 1800–600 cm\(^{-1}\) at 183 K. These spectra were identical within experimental limits of error (not shown here).

C. \(T_1\) RR Spectra at 183 K. Time-resolved RR spectra of the lowest triplet state of 1,3,5-hexatriene and deuteriated derivatives obtained by subtraction procedures are shown in Figure 4. Spectrum 4A was obtained from EHT in methanol (solution 3) at 183 K, spectrum 4B from (E)-HT-3-d in CD\(_3\)CN at 183 K, spectrum 4C from (E)-HT-3-d in cyclopentane (solution 5) at 183 K, and spectrum 4D from (E)-HT-1,1-d\(_d\) in cyclopentane (solution 6) at 183 K. The frequencies of the triplet bands observed in Figure 4 are listed in Table II for EHT, (E)-HT-3-d, and (E)-HT-1,1-d\(_d\). Previously published values for (E)-HT-3,4-d\(_d\), and (E)-HT-2,5-d\(_d\) are listed in Table II as well.

In Figure 4A an artifact is observed at 1034 cm\(^{-1}\) due to the strong methanol band at this frequency, in parts C and D of Figure 4, artifacts are observed at 886 cm\(^{-1}\) due to cyclopentane, and in Figure 4B artifacts are observed at 832 and 348 cm\(^{-1}\) due to strong CD\(_3\)CN bands. Spectra 4A, 4C, and 4D are shown below in Figures 5–7, respectively, together with the corresponding theoretical spectra.

D. Temperature Dependence of \(T_1\), Lifetime. The decay kinetics of triplet 1,3,5-hexatriene at low temperature was investigated by varying the delay between the pump-and-probe laser pulses. For EHT in cyclopentane (solution 1) at 183 K, we measured the intensity of the strong transient band at 1574 cm\(^{-1}\) relative to the intensity of the solvent bands at 1446 and 1028 cm\(^{-1}\) for pump-probe time delays of 80, 150, 250, 350, and 450 ns. For EHT in methanol (solution 3) at 189 K, we measured the intensity of the 1574-cm\(^{-1}\) band relative to the intensity of the solvent bands.
Figure 4. Triplet-state time-resolved resonance Raman spectra of Ar-saturated solutions of (A) methanol, 0.817 M acetone, 0.012 M EHT; (B) acetonitrile-d$_3$, 0.545 M acetone, 0.005 M (E)-HT-3-d; (C) cyclopentane, 0.408 M acetone, 0.011 M (E)-HT-3-d; and (D) cyclopentane, 0.408 M acetone, 0.009 M (E)-HT-1,1-d$_3$. Solvent, acetone, and hexatriene ground-state bands subtracted. Temperature: A, C, and D 183 K; B 237 K. Pump wavelength 308 nm, probe wavelength 315 nm. Pump–probe delay 80 ns.

Figure 5. Calculated wavenumbers and relative $\gamma$ values for the totally symmetric vibrational modes of the E form of 1,3,5-hexatriene in resonance with the T$_1$ → T$_3$ transition, the Z form (T$_1$ → T$_3$), and the sum of the E and Z forms, together with the experimental triplet-state time-resolved resonance Raman spectrum obtained at 183 K (same spectrum as Figure 4A).

Figure 6. Calculated wavenumbers and relative $\gamma$ values for the totally symmetric vibrational modes of the E form of 3-deuterio-1,3,5-hexatriene in resonance with the T$_1$ → T$_3$ transition, the Z form (T$_1$ → T$_3$), and the sum of the E and Z forms, together with the experimental triplet-state time-resolved resonance Raman spectrum obtained at 183 K (same spectrum as Figure 4C).

Figure 7. Calculated wavenumbers and relative $\gamma$ values for the totally symmetric vibrational modes of the E form of 1,1-dideuterio-1,3,5-hexatriene in resonance with the T$_1$ → T$_3$ transition, the Z form (T$_1$ → T$_3$), and the sum of the E and Z forms, together with the experimental triplet-state time-resolved resonance Raman spectrum obtained at 183 K (same spectrum as Figure 4D).

Although the decay curves for solutions 1 and 3 were similar, the buildup of T$_1$ 1,3,5-hexatriene by energy transfer from acetone was different for the two solutions. In cyclopentane (solution 1), maximum absorbance was reached before 80 ns, and in methanol (solution 3) between 110 and 210 ns.

Data from time-resolved triplet–triplet absorption measurements at 318 nm of EHT in methanol (solution 8), are shown in Figure...
8. At all temperatures, logarithmic plots of triplet-triplet absorption as a function of time yielded straight lines, corresponding to decay rate constants of $4.90 \times 10^5$ s$^{-1}$ at 296 K, $3.99 \times 10^5$ s$^{-1}$ at 244 K, 3.11 $\times 10^6$ s$^{-1}$ at 207 K, and 2.43 $\times 10^6$ s$^{-1}$ at 183 K. The Arrhenius plot in Figure 8 yields an activation energy of 0.7 $\pm$ 0.2 kcal/mol and a frequency factor of (1.6 $\pm$ 0.3) $\times 10^{12}$ s$^{-1}$. The first-order decay of the triplet-triplet absorption at 183 K is illustrated by the inset in Figure 8. An increase in the buildup time of TI, 1,3,5-hexatriene was clearly observed with decreasing temperature (not shown).

IV. Theoretical Results

A detailed account of the theoretical calculations for HT, HT-3-d, HT-3,4-d$_2$, and HT-2,5-d$_2$ has been given previously.$^2$ Only the most essential results shall be summarized briefly. According to the QCFF/PI calculations, relative minima were found at the planar E and planar Z geometries of the lowest triplet state of 1,3,5-hexatriene. After geometry optimization, the planar Z form was computed at 1.1 kcal/mol above the energy of the planar E form, and the geometry perpendicular or twisted (Tw) around the central CC bond at 7.1 kcal/mol above the planar E form. Only one strong $T_1 \rightarrow T_2$ ($\nu = 5, 6$) transition was computed in the wavelength region of the present experiments for each of the three (E, Z, and Tw) forms. The $T_2 \rightarrow T_1$ transitions of the E and Z forms were calculated to be in resonance with the exciting laser wavelength, while that of the Tw form was off-resonance by approximately 1 eV. On the basis of these results and a careful comparison of calculated and experimental TI, RR spectra, it was concluded that only the planar E and Z forms contribute to the $T_1$, RR spectra.

The complete sets of computed wavenumbers and normal modes of the three $T_1$ forms have been reported previously for HT, HT-3,4-d$_2$, and HT-2,5-d$_2$.$^2$ Also reported were the Stokes shift parameters $\gamma$ of the totally symmetric vibrational modes in $T_1$, which are related to geometry changes between $T_1$ and $T_2$ ($\nu = 5, 6$)

$$\gamma = \frac{\omega}{\nu} (\Delta Q)^2$$  \hspace{1cm} (1)

where $\omega$ is the vibrational frequency (rad/s), and $\Delta Q_i$ is the projection onto the ith normal coordinate of $T_1$, of the equilibrium geometry change between $T_1$ and $T_2$. These parameters are proportional to the Franck-Condon (FC) intensities of totally symmetric modes when the exciting beam is roughly in resonance with the origin of the $T_1 \rightarrow T_2$ transition.

In the present paper, we report the computed wavenumbers and Stokes shift parameters $\gamma$ of the totally symmetric vibrational modes of the lowest triplet state of HT-3-d and HT-1,1-d$_2$, together with the previously reported values for HT, in the planar E geometry (Table III), in the planar Z geometry (Table IV), and in the Tw geometry (Table V). All calculations were performed using the QCFF/PI program as described previously.$^2$ In Figures 5–7, we have plotted the calculated $\gamma$ values for the planar E and planar Z forms of HT, HT-3-d, and HT-1,1-d$_2$, as a function of frequency together with the experimentally obtained RR spectra in the $T_1$ state.

Finally, we present in Figure 9 the internal coordinate contribution to the normal modes of 1,3,5-hexatriene in the $T_1$ state for certain characteristic modes of the planar E and Z forms.

V. Discussion

The spectra shown in Figures 2 and 3 are obtained in methanol, whereas previous experiments were performed in acetonitrile and cyclopentane. The reason for not using acetonitrile in the present work is its relatively high melting point (227 K), and in cyclopentane, due to some yet unknown reason, the room-temperature spectra were of relatively low signal-to-noise ratio.$^1$ As methanol has a low melting point (175 K), and methanol solutions show good $T_1$ RR spectra at 293 K, this was the solvent chosen for a comparison of spectra obtained at different temperatures. One

may then ask whether the short-lived species or mixture of species observed in the T₁ state of 1,3,5-hexatriene at 293 K is the same in different solvents. All bands observed previously in acetonitrile solution are observed in methanol in the present study as well. In addition, a number of hitherto unobserved vibrational bands (at 1332, 959, 780, 600, and 341 cm⁻¹) are found in the present study at 293 K. Of these, a band around 600 cm⁻¹ has been noted doubtful in acetonitrile previously, and the newly observed band at 341 cm⁻¹ was probably masked by a solvent band (379 cm⁻¹) which are below the detection limit at 293 K, are observed in previous experiments. Hence, we conclude that the present T₁ lifetimes are observed in methanol in the present study as well.

Table V: Computed Wavenumbers (cm⁻¹) and Stokes Shift Parameters γ for the T₁ - T₀ Transition of Totally Symmetric Normal Modes of 29° Twisted (Tw) 1,3,5-Hexatriene

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Figure 9. Internal coordinate composition of characteristic normal modes of the planar E and Z forms of 1,3,5-hexatriene in the T₁ state. Numbers indicate calculated wavenumbers (cm⁻¹).

In our previous studies,¹,² we concluded on the basis of room-temperature spectra that an equilibrium between different forms is established on the T₁ PES within the lifetime of T₁. Two forms, namely, the planar E and Z forms, were found to contribute to the T₁ RR spectra, while a contribution of the twisted form could not be proved. Furthermore, the calculations suggested that the energies of the relaxed E and Z forms are similar, and that the resonance scattering conditions (detuning from the 0-0 transition) are approximately the same for the two forms. They can, however, according to the calculations, be distinguished by their different contributions to the RR spectrum of the equilibrium mixture. In particular, the band at 1270 cm⁻¹ was attributed to the Z and the band at 1106 cm⁻¹ to the E form. If this picture is accepted, what is then the effect of lowering the temperature?

The observation of identical T₁ RR spectra at 183 K starting from either the EHT or ZHT ground-state isomer indicates that a full equilibration is attained along the torsional coordinate during the T₁ lifetime. Then, the relative populations of the energy minima at the E and Z geometries will reflect the energy difference between the two forms, according to a Boltzmann distribution

\[ n₁/n₂ = e^{(Δν/Δν) (h/Δν)} \]

where \( k_B \) is the Boltzmann constant and \( n₁ \) and \( n₂ \) are the equilibrium populations at the minima (E) and (Z). If the two forms are isoeNERGETIC, no changes in relative population will occur upon lowering the temperature, whereas the larger their energy difference is, the larger will be the change in the population ratio. Obviously, if the energy difference is larger (≥3 kcal/mol), the less stable form will be present in a tiny fraction at both temperatures, and hence, only the more stable form will contribute effectively to the observed RR spectrum. Experimentally, the RR spectra of Figure 3 reveal no distinct change in the relative intensities of the 1270- and 1106-cm⁻¹ bands, when going from 293 to 183 K.

According to our QCF/PI calculations,² the planar Z form is situated at 1.1 kcal/mol above the planar E form, corresponding to a ratio of planar Z to planar E triplet of 0.15 at 293 K and 0.05 at 183 K. Such a change is definitely not observed in the spectra. We estimate that as a lower limit a relative change of 25% would clearly be observable. Assuming that the planar E triplet is below planar Z in energy, and that the E/Z ratio at 183 K is ≤1.25 times the ratio at 293 K, eq 2 yields an upper limit of 0.22 kcal/mol for the energy difference between the planar E and Z forms. This conclusion rests on the band assignment given for the 1270- and 1106-cm⁻¹ bands. We shall see below that this assignment is strongly supported by the new results from deuterated derivatives.

We now turn to the question of the torsional energy barriers on the T₁ PES. Within experimental limits of error, identical T₁ RR spectra are observed for EHT and ZHT at a pump-probe time delay of 80 ns, and no changes in relative intensities of vibrational bands are observed for longer time delays. If the T₁ PES has two minima separated by an energy barrier \( E_b \), the rate constant \( k \) for the process leading from one minimum to the other can be expressed as

\[ k = (k_B T/h) e^{(-E_b/k_B T)} \]

where \( k_B \) is the Boltzmann constant and \( h \) is Planck's constant. Since at 183 K equilibration between the E and Z forms is reached in ≤80 ns, \( E_b \) must be ≤4.6 kcal/mol. Possibly, friction would further slow down the motion on the T₁ PES and contribute its own activation energy. Thus, it follows that the activation energy derived from eq 3 is a fortiori an upper limit to the T₁ intrinsic intramolecular energy barrier for torsion.

The upper limits of 4.6 kcal/mol for the barrier \( E_b \) between the E and Z forms, and of 0.22 kcal/mol for the energy difference of the E and Z forms, together indicate a rather flat PES with...
respect to motion along the torsional coordinate of the central CC bond of HT in T₁. This is expected on the basis of the calculated C₂C₃ bond lengths of 1.470 (E form) and 1.472 Å (Z form) in T₁, which corresponds to the length of the ground-state CC single bond (experimental C₂C₃ bond length 1.458 Å for EHT, 1.462 Å for ZHT).  

### Table VI: Tentative assignment of experimental (Table II) to calculated Raman spectra (cm⁻¹) of the lowest excited triplet state of EHT, (E)-HT-3-d, and (E)-HT-1,1-d₂

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*E, Table III; Z, Table IV.

*E, Table III; Z, Table IV.

The Journal of Physical Chemistry, Vol. 95, No. 18, 1991 6891
as estimated above. Moreover, mainly on the basis of the less favorable resonance conditions, we believe that a contribution of the Tw form is unlikely. However, to tell whether the Tw form is present or not, additional experiments with a probe laser wavelength around 220 nm (T₁ → T₂ transition of the Tw form) are necessary.

An important consequence of the above assignment of the triplet spectra is that the strong band observed at 1271 cm⁻¹ for non-deuterated, non-methylated 1,3,5-hexatriene, and assigned to CH rock coupled to C–C stretch, is indicative of the planar Z form. We may thus have a spectral feature that shows whether the planar Z form is present in the triplet state, a Z band. This rule may be applicable to other polyenes: For the T₁ state of retinal and retinylidenecacetaldehydes, Hashimoto et al. assigned a Raman band around 1265 cm⁻¹ to the CH bend at a nonmethylated C=C double bond.

Some points should be made with respect to the normal modes shown in Figure 9 for T₁, T₂, and T₃, where 1,3,5-hexatriene. For EHT, the two strongest T₁ modes, calculated at 1554 and 1154 cm⁻¹, are rotated (Duschinsky effect) with respect to the S₀ modes calculated at 1558 and 1197 cm⁻¹ in ref 12. The T₁ 1554 cm⁻¹ mode has major contributions from C₁C₂, C₃C₄, and C₅C₆ stretches, corresponding to the 1558 cm⁻¹ S₀ mode. The T₁ 1154 cm⁻¹ mode is dominated by C₃C₄ and C₅C₆ stretches, corresponding to the S₀ 1197 cm⁻¹ mode. For ZHT, a similar rotation of the T₁ 1207 cm⁻¹ mode is observed with respect to the S₀ 1548 cm⁻¹ mode. For the T₁ 1539 cm⁻¹ mode, the rotation is more complicated. The high observed intensity of the modes depicted in Figure 9, in particular of the 1290 cm⁻¹ band, is mainly due to their CC stretch components. The phase of the local CC stretches in these normal modes is the same as the phase of the CC bond length changes in the T₁-T₂ geometry change, localized mainly in the C₁C₂, C₃C₄, and C₅C₆ bond lengths.

The present triplet Raman spectra of HT-3-d and HT-1,1-d₂ have a richer vibrational structure than HT because of their lower symmetry. Ground-state (E)-1,3,5-hexatriene and also the planar E triplet transform according to C₂ symmetry and so obey the exclusion principle between Raman and infrared-active vibrations. Deuteration in the 3-position ((E)-HT-3-d, and the EHT band at 1321 cm⁻¹) lowers the symmetry to C₃ and so should lead to a breakdown of the exclusion principle. This is indeed observed when the calculated triplet spectra of EHT and (E)-HT-3-d are compared, where the EHT bands at 1193 and 1154 cm⁻¹ distribute their intensity among the 1221-, 1166-, and 1141-cm⁻¹ bands of (E)-HT-3-d, and the EHT band at 939 cm⁻¹ splits into the 1003- and 902-cm⁻¹ bands of (E)-HT-3-d. Most of these bands are dominated by CH (CD) rock. Similar considerations apply to the planar Z form, where deuteration in the 3-position lowers the symmetry from C₃ to C₂. For the planar Z form, the HT band at 1207 cm⁻¹ splits into the 1237- and 1168-cm⁻¹ bands of HT-3-d, and the HT band at 893 cm⁻¹ splits its intensity between the 985- and 907-cm⁻¹ bands of HT-3-d. For HT-1,1-d₂ compared to HT, the EHT band at 1321 cm⁻¹ splits into the 1323- and 1310-cm⁻¹ bands of (E)-HT-1,1-d₂, whereas for the planar Z form, additional bands appear around 1300, 1100, 1000, 750, and 400 cm⁻¹ in the calculated spectra of (Z)-HT-1,1-d₂.

D. Intensity of T₁ RR Spectra. We shall next address the question of why the triplet Raman spectra are so much stronger at 183 K than at 293 K. From Figures 2 and 3 it is seen that the peak height of the triplet spectra increases 4 times higher at 183 K and 80-ns delay than at 293 K and 60-ns delay. Several possible explanations exist for this phenomenon:

First, it is seen from Figures 2 and 3 that the triplet Raman bandwidth decreases from 293 to 183 K, so the difference in the integrated band intensities is smaller than the factor 4; this effect is most pronounced for the 1574-cm⁻¹ band. Second, due to the longer triplet lifetime at 183 K (see below), the maximum triplet concentration is higher. Third, the triplet–triplet absorption spectrum with a local maximum around 315 nm in toluene at room temperature is likely to have a smaller bandwidth at 183 K and a higher extinction coefficient at 315 nm, leading to stronger resonance enhancement of the triplet Raman spectrum. Fourth, the increased Raman intensity at 183 K may be due to a different distribution between triplet geometries. If the planar E and Z forms alone give rise to RR spectra, and the Tw form is at higher energy than the planar forms, then lowering the temperature should lead to an increase in the relative amount of the planar forms and consequently in the Raman intensities.

In contrast, if the energy of the Tw form were significantly below the energy of the planar forms, the ratio of the planar forms to the Tw form would decrease at lower temperature, leading to weaker triplet Raman spectra. The strong Raman spectra observed at 183 K indicate that the Tw form cannot be much lower in energy than the planar forms. We estimate the upper limit of the E(planar)−E(Tw) energy difference to be 1 kcal/mol. The estimated activation energy E_a of the triplet decay (see below) sets an upper limit for the energy of the Tw form relative to the planar forms of 0.7 kcal/mol.

E. Kinetics of Formation and Decay of the T₁ State. We now turn to the kinetics of the T₁ state. When comparing the kinetics at 293 and 183 K, one has to keep in mind that differences observed may be due to pure temperature effects, but may also be due to changes in viscosity accompanying the temperature changes. Experimental kinetics of formation and decay of EHT in T₁, based on RR observations, were reported above; the first-order decay rate constant was 10.9 X 10⁶ s⁻¹ in anentorcoline at 293 K. 4.0 X 10⁶ s⁻¹ in cyclopentane at 183 K, and 3.8 X 10⁶ s⁻¹ in methanol at 189 K. Data based on time-resolved absorption measurements are shown in Figure 8. It is seen from Figure 8 that the T₁ lifetime increases by a factor of 2 when going from 293 to 183 K. One may then ask whether this is an effect of temperature, viscosity, or both. The viscosity of acetonitrile is 0.369 cp at 290.4 K,¹⁵ that of cyclopentane is 0.31 cp at 183 K,¹⁶ and that of methanol is 0.68 cp at 189 K.¹⁷ From the very similar decay rate constants observed in the RR experiments from methanol and cyclopentane, i.e., solutions at similar temperature but considerably different viscosity, it seems most likely that in the present experiments the temperature is the main factor determining the T₁ decay rate. Accepting this view, and assuming an Arrhenius dependence

\[ k = A e^{-E_a/k_b T} \]  (4)

doing the data in Figure 8 yield an activation energy of E_a = 0.7 ± 0.2 kcal/mol and a frequency factor of A = (1.6 ± 0.3) X 10¹⁶ s⁻¹ for the decay of T₁, HT.

The value of the frequency factor does not pertain to the motion on the T₁ PES for which a value of ca. 10¹⁲ s⁻¹ would be expected from eq 3, in agreement with experiments on related systems.¹⁸,¹⁹ Rather, it is characteristic of a spin-forbidden, radiationless T₁ → S₀ intersystem-crossing (ISC) process.¹⁰,¹⁸ The low value of the activation energy suggests that planar and twisted forms are roughly degenerate.

The effect of viscosity, on the other hand, is observable in the slow formation rate of the triplet state in methanol as compared to cyclopentane mentioned above. The formation of T₁, HT occurs by exothermic triplet energy transfer from acetone, i.e., a bimolecular interaction.
The formation rate of the twisted form, if below the planar forms, to be at most 1.0 kcal/mol below these. Even if populated to a considerable degree, this Tw form would probably contribute little to the observed RR spectra, due to less favorable resonance conditions.

Torso-sional equilibration on the Tw PES occurs much faster than the decay of the triplet population. From the fact that equilibration between the E and Z forms is established at 183 K before 80 ns, we estimated an upper limit of 4.6 kcal/mol for energy barriers between the planar E and Z forms with respect to the torsional coordinate around the central CC bond on the T1 PES. The Tw form must then also be at most 4.6 kcal/mol above the planar forms. From the dependence of triplet-state lifetime on temperature, we obtained an activation energy of triplet decay of 0.7 kcal/mol. This must also be an upper limit for the energy difference on the T1 PES between the planar and the twisted forms.

Little is known about the energy gap between the T1 and S0 PES. A maximum on the S0 PES of 1,3,5-hexatriene of 47.5 kcal/mol (46.1 kcal/mol) with respect to the E(Z) form has been calculated at 90° twist around the central CC bond. Experimentally, the activation energy E_A for thermal isomerization of EHT to ZHT has been determined as 43.3 kcal/mol in the gas phase. The vertical triplet energy, obtained from the most intense band of the S0 → T1 absorption spectrum, is 59.4 kcal/mol for EHT and 60.8 kcal/mol for ZHT. The 0–0 energy gap, derived from the first feature of the S0 → T1 absorption spectrum, is 46.9 and 47.7 kcal/mol for EHT and ZHT, respectively. These 0–0 energies are determined with an uncertainty of at least 0.5 kcal/mol. Thus, we can infer only that the relaxed E form has an energy slightly below the energy of the Z form.

For ZHT being 1.4 kcal/mol above EHT in S0 (theory, ref 22), and the S0–T1 0–0 energy gap being 0.8 kcal/mol larger for ZHT than for EHT (experiment, ref 24), the Z form is expected to be 2.2 kcal/mol above the planar E form in T1. This is in contrast with the present finding of the E(Z) forms being within 0.22 kcal/mol in energy in T1. The reason for this discrepancy is probably that the different methods probe molecules with different degrees of relaxation. Relaxation takes place in T1 by torsion around the CC6C4 bond, this being the weakest CC bond in T1, as reflected in the slight nonplanarity of the Z form, and in particular by changes in CC bond lengths and CCC in-plane bond angles.

There is no distinct measure of the T1 energy at the Tw geometry. However, the temperature-dependent data presented above suggest that the energy of the Tw form in T1 lies within 1 kcal/mol from the energy of the E form. Thus, the T1–S0 energy gap at 90° is expected to be less than 5 kcal/mol. Although a crossing between the S0 and T1 PES in the T region cannot be ruled out, it appears unlikely in view of the data presented above.

The T1 decay at the Tw geometry is much faster than at planar geometries because of the reduced energy gap and the increase of the S0–T1 spin-orbit coupling. Model calculations on stilbene showed that, for T1–S0 energy gaps smaller than 4 kcal/mol, the decay rate constant at 90° is ca. 10^4 s^{-1}, in substantial agreement with the experimental observation. In contrast, if the T1 → S0 decay were to take place at the planar geometries, the T1 lifetime would be in the order of 10 ms. For the HT case, the observed triplet lifetimes of 100–300 ns clearly correspond to a decay occurring close to the Tw geometry.

As we have shown above, the temperature dependence of the decay rate of triplet HT can be described by an Arrhenius equation. An attractively simple interpretation of the observed activation energy is that it corresponds to the temperature effect on the equilibrium distribution of planar and twisted forms, the latter being ca. 0.7 kcal/mol higher in energy. The decay rate at the twisted geometry is then the observed frequency factor divided by the population of the twisted form. Alternatively, the temperature effect may be ascribed to the process of reaching a

Figure 10. Qualitative potential energy surfaces (PES) of T1 and S0 1,3,5-hexatriene for the torsional reaction coordinate of the central CC bond, with (A) and without (B) a local minimum at the 90° twisted geometry.
critical (not necessarily stationary) point on the PES, ca. 0.7 kcal/mol higher in energy than the planar E form, where the T₁→S₀ crossing occurs (see Figure 10B). In this view, the frequency factor simply corresponds to the T₁→S₀ ISC rate at the crossing geometry. In either case, a firm conclusion from our work is that the twisted species cannot be much higher in energy than the planar forms.

For the twisted form being 0.7 kcal/mol above the E and Z forms, the Boltzmann distribution, eq 2, yields a planar/twisted population ratio of 1:0.15 at 183 K, and 1:0.30 at 293 K. With the different resonance conditions, observation of the twisted form in the RR spectra is rather unlikely, as estimated in ref 27.

From the validity of the nonequilibration of excited rotamers (NEER) principle in the T₁ state of 2,5-dimethyl-1,3,5-hexatriene, we have estimated a lower limit of the rotational barrier around the C₂C₃ bond of more than 8 kcal/mol. Most likely, this barrier is similar for 1,3,5-hexatriene, and it is definitely higher than the barrier for the twisting of the central CC bond. This agrees with the computed lengths of the CC bonds in T₁. The optimized length of the C₂C₃ bond is 1.386 Å, while the calculated C₂C₄ bond length is 1.470 Å. Thus, the T₁ PES of EHT for the twisting of the C₂C₃ bond has minima at the zEt (Chart 1) and zEc geometries, which are separated by a barrier higher than 8 kcal/mol. Similar considerations apply to the zEt and zEc geometries.

We now want to relate the present picture of the T₁ PES of 1,3,5-hexatriene to recent studies of the T₁ PES of 1,2-diarylethenes and of arylethenenes. For adiabatic mechanisms, isomerization takes place on the T₁ PES, followed by a vertical decay to the S₀ PES at one of the planar geometries. For diabatic mechanisms, equilibration takes place on the T₁ PES, followed by decay by 90° to the S₀ barrier, from where isomerization proceeds by relaxation to the E or Z forms. The factors that favor one or the other mechanism have been discussed recently.

In both cases, equilibration takes place on the T₁ PES within the triplet lifetime, and planar geometries are substantially populated. For the diarylethenes, where the adiabatic mechanism applies, the electronic T₁ state corresponds to an excitation localized on the aromatic moieties. Therefore, the barrier to torsion on the T₁ PES is sufficiently high in these compounds so that the decay takes place predominantly at the planar geometries, and because of an energy gap in the order of 40 kcal/mol, the T₁ lifetime is long (>1 ms). Since decay takes place from a planar T₁ geometry, a planar S₀ minimum is possible, and no further reaction takes place.

In 1,3,5-hexatriene, as well as in stilbene, the T₁ excitation is largely localized on the central C=C double bond. Hence, the T₁ PES has a low barrier or a minimum at 90°. Consequently, although planar geometries are predominant, decay takes place at the T₁w geometry, where the T₁→S₀ energy gap is small. However, since at the T₁w geometry the S₀ PES has a maximum, the molecules relax to both planar E and planar Z S₀ geometries, thus giving rise to a diabatic photoisomerization.

Thus, the division of photo reactions into adiabatic and diabatic ones is strictly related to the amount of excitation localized on the central C=C double bond and hence to the size of the chromophores linked to this bond.

VI. Conclusions

In the present paper we have obtained time-resolved RR spectra of the lowest excited triplet state of 1,3,5-hexatriene and its 3-deuterio and 1,1-dideuterio derivatives in solution at 183 K. We have shown that it is possible to obtain spectra under these conditions, and that the quality of the spectra is improved strongly at low temperature.

We have calculated the T₁ RR spectra for the planar E and Z geometries of the three molecules, and for the geometry that is perpendicular (T₁w) at the central CC bond. For each of the three geometries we have identified the strongest T₁→T₁ tran- 
sition and calculated the RR intensities on the basis of geometry changes between T₁ and T₁w.

Comparing with the theoretical spectra, we have assigned the observed RR spectra to the planar E and planar Z geometries, the two geometries being nearly equally populated. For 3-deuterio-1,3,5-hexatriene and 1,1-dideuterio-1,3,5-hexatriene, the assignment between theoretical and experimental spectra is nearly unambiguous, a result which establishes that time-resolved RR spectroscopy in connection with theoretical calculations is a valuable method to determine excited-state molecular structure. In particular, we have shown that a strong triplet Raman band around 1270 cm⁻¹ is diagnostic of the planar Z geometry.

From comparison of T₁ RR spectra at 293 and 183 K, we have estimated that the E and Z forms are virtually degenerate, and that the T₁w geometry probably is above, and definitely less than 1.0 kcal/mol below, the planar forms. We have measured the triplet–triplet absorption of 1,3,5-hexatriene as a function of temperature; this measurement allows estimation of the frequency factor at ca. 10⁷ s⁻¹, a value that agrees with the notion that the rate-determining step of T₁ decay is the T₁→S₀ ISC. Viscosity effects are seen at 183 K for the buildup of T₁ at 3,5-hexatriene by energy transfer from a sensitizer, but not for the decay of the T₁w state.

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