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UV absorption and Raman Spectra of the ground states and time-resolved resonance Raman Spectra of the lowest excited triplet states of the E and Z isomers of 2,5-dimethyl-1,3,5-hexatriene. indication of nonequilibration of excited rotamers in the lowest triplet state

Langkilde, F.W.; Jensen, N.-H.; Wilbrandt, R.; Brouwer, A.M.; Jacobs, H.J.C.

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is, at the top of the barrier. As δ' increases to 90° and finally back to the minimum at 120° , the radical center moves back across the CCC plane and returns to its former position when δ' was 0° . Thus, although the out-of-plane bending angle γ changes considerably during the relaxed in-phase internal rotation, the coupled motion does not affect the barrier height to the same degree as was previously demonstrated for the out-of-phase rotation.

The dramatic differences between energy paths for the relaxed in- and out-of-phase double internal rotations are attributed to steric interactions between the methyl groups during the internal rotation. Consider the geometries for the two transition states shown in Figure 6, ($\delta = 110^\circ$) and Figure 8 ($\delta' = 60^\circ$). The former is only 0.30 kcal/mol while the latter is 1.05 kcal/mol above the minimum energy. Note that the hydrogens H32 and H21 (Figure 8) are forced to point toward each other, a situation that involves more steric interaction than the in-plane hydrogens, H31 and H21, in the $\delta = 110^\circ$ structure shown in Figure 6. For the most part the two geometries are related to each other by a 180° rotation of the methyl groups. Again the geometry much higher in energy has in-plane CH bonds pointing toward each other; the geometry with the lower energy manages to minimize this interaction by having the in-plane hydrogens pointing away from each other.

Summary

The geometry of the isopropyl radical was optimized by using restricted open-shell Hartree-Fock calculations. Although a number of geometries had small gradients, only one was a min-

imum on the energy surface. The geometry corresponding to this minimum contains only one plane of symmetry with the two methyl groups located off the plane and the α -CH bond in the plane of symmetry. Barriers for internal rotation of a single methyl group and internal rotation of two methyl groups were investigated. The latter motions were set up to conform to the C_2 point group symmetry of the radical. A threefold potential function was computed for the single methyl internal rotation with a barrier height of 1.08 and 0.8 kcal/mol for the rigid and relaxed motions. A threefold potential function was also found for the in-phase double internal rotation with barriers equal to 2.27 and 1.05 kcal/mol for the rigid and relaxed modes. The out-of-phase double internal rotation for the rigid case has a threefold symmetry with a barrier height of 2.27 kcal/mol. The energy path for the relaxed rotation has two barriers between 0° and 120° ; the first is at 1.08 kcal/mol while the second is much lower at 0.30 kcal/mol.

The geometric changes found during the relaxed internal rotations indicated that there is extensive coupling between internal rotation and the out-of-plane bending of the radical center. For the relaxed single methyl and in-phase double methyl rotations the coupling lowers the barrier heights but does not alter the threefold symmetry. However, during the out-of-phase rotation a transition-state geometry is formed that minimizes steric interactions between in-plane hydrogen atoms. Since the energy of this transition state is only slightly above the minimum, 0.3 kcal/mol, the radical experiences almost free rotation over a relatively large range of δ .

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UV Absorption and Raman Spectra of the Ground States and Time-Resolved Resonance Raman Spectra of the Lowest Excited Triplet States of the E and Z Isomers of 2,5-Dimethyl-1,3,5-hexatriene. Indication of Nonequilibrium of Excited Rotamers in the Lowest Triplet State

Frans W. Langkilde, Niels-Henrik Jensen, Robert Wilbrandt,*

Chemistry Department, Riso National Laboratory, DK-4000 Roskilde, Denmark

Albert M. Brouwer, and Harry J. C. Jacobs

Department of Chemistry, State University at Leiden, 2300 RA Leiden, The Netherlands

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The UV absorption spectra and Raman spectra of the ground states and the time-resolved resonance Raman spectra of the lowest excited triplet states of the E and Z isomers of 2,5-dimethyl-1,3,5-hexatriene are reported. The ground-state spectra support previously suggested differences in the C_2-C_3 and C_4-C_5 single-bond conformations of the two isomers, the E isomer having a planar tEt and the Z isomer predominantly a nonplanar cZc conformation. The time-resolved Raman spectra are obtained in a flash photolysis experiment using two pulsed lasers in a pump-probe arrangement. The lowest triplet states of the trienes are populated by excitation of acetone and subsequent triplet energy transfer to the trienes. Raman bands from the triplet state are found at 1551, 1389, 1357, and 1146 cm^{-1} for the E isomer and at 1548, 1350, and 1151 cm^{-1} for the Z isomer. A partial assignment of these spectra is proposed by comparison with similar spectra of hexatriene, heptatriene, and octatriene, and the relaxed triplet geometries of 2,5-dimethyl-1,3,5-hexatriene are discussed. The triplet Raman spectra from the two isomers of 2,5-dimethyl-1,3,5-hexatriene are very similar, though not identical. The results are discussed on the basis of the NEER (nonequilibrium of excited rotamers) principle, which was suggested previously to apply to the excited singlet states of the two isomers. The experimental findings suggest that the validity of the NEER principle can be extended to excited triplet states and consequently to much longer lifetimes. From this a lower limit of the rotational barrier around the formal single bonds in the triplet state is estimated to be 35 kJ/mol.

Introduction

The E-Z isomerization of linear polyenes is one of the simplest photochemical reactions.¹ For an understanding of this process it is necessary to study stable products as well as short-lived

intermediates. Of all systems studied stilbene has been most thoroughly investigated.² As the lowest excited triplet state is an intermediate in the sensitized photoisomerization of many polyenes,²⁻⁶ a detailed understanding of the T_1 potential energy surface

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with respect to twisting around double bonds is of importance and has been addressed for longer polyenes with varying results.

For β -carotene transient resonance Raman spectra of the lowest triplet states produced from the all-E isomer⁷ and the 15-Z isomer⁸ were found to be similar. However, HPLC analysis of primary products from sensitized photoisomerization indicates that the 15-Z isomer of β -carotene produces the all-E isomer alone, whereas the all-E isomer produces both the 15-Z, the 9-Z, and the 13-Z isomers.⁶ Teraoka et al.^{9,10} have obtained transient Raman spectra of the triplet states produced from the all-E, 9-Z, 13-Z, and 15-Z isomers. These authors conclude that the triplet Raman spectra of the isomers are similar, indicating a common triplet configuration for β -carotene isomers.

For retinal, one study¹¹ concludes on the basis of transient absorption and resonance Raman spectroscopy that the 9-Z, 11-Z, 13-Z, and all-E isomers form either different relaxed triplet species or different mixtures of relaxed triplet species following triplet energy transfer from a sensitizer in pulse radiolysis experiments. Another study¹² concludes from transient Raman spectroscopy that the 7-Z, 9-Z, 11-Z, and all-E isomers of retinal form an identical relaxed triplet species upon photoexcitation and subsequent intersystem crossing, whereas the 13-Z isomer forms a different relaxed triplet species. Karatsu et al.¹³ have studied the triplet intermediates in the sensitized photoisomerization of 2-styrylanthracene by transient absorption spectroscopy. For this aromatic polyene they found identical $T_n \leftarrow T_1$ absorption spectra for the E and Z isomers and suggested a planar triplet configuration. Hamaguchi¹⁴ found identical transient resonance Raman spectra for the triplet intermediates produced from the same two isomers.

As seen from the above survey no clear picture exists of the nature of the T_1 potential energy surface with respect to twisting around double bonds in polyenes, and the question whether different isomers produce identical or different relaxed triplet species is still unanswered for most systems. The E and Z isomers of 2,5-dimethyl-1,3,5-hexatriene are obvious model compounds to study in a further effort to understand the nature of the T_1 potential energy surface. As discussed below the methyl groups induce steric hindrance in the Z isomer, which influences the ground-state geometry strongly. With their ground-state geometries being so dissimilar it is of great interest to probe the nature of the conformationally relaxed triplet intermediates produced by energy transfer from an excited triplet sensitizer to each of the two isomers.

Theoretical studies of energies and equilibrium geometries of excited states of (E)-1,3,5-hexatriene have been reported by several authors. Lasaga et al.¹⁵ have used an empirical function for the potential of the σ electrons and a modified PPP model with CI through double excitations for the π electrons to study the two

lowest excited singlet states of hexatriene, under the assumption of planar excited-state geometries. For both the $2^1A_g^-$ and the $1^1B_u^+$ states the C_1-C_2 and C_2-C_3 bonds were found to be of equal lengths, whereas the C_3-C_4 bond was significantly longer.

Bonačić-Koutecký and Ishimaru¹⁶ have performed ab initio calculations on energies and equilibrium geometries of the T_1 state of hexatriene. They found that three forms were close in energy and possible intermediates in the E-Z isomerization of hexatriene: diallylic (I), methylenepentadienyl (II), and the planar 1,6-diradical (III).

Ohmine and Morokuma¹⁷ have performed both ab initio and MINDO/3 calculations on the T_1 state of hexatriene. With the MINDO/3 procedure they found that a geometry with twisting around the central $C=C$ bond is 5.8 kcal/mol lower in energy than the planar geometry, whereas a geometry with twisting around a terminal $C=C$ bond was found to be 1.1 kcal/mol lower than the planar geometry.

Said et al.¹ used a nonempirical Heisenberg Hamiltonian and found the geometry with twisting around the central $C=C$ bond to be 1.7 kcal/mol lower in energy than the planar geometry, whereas the geometry with twisting around a terminal $C=C$ bond was found to be 3.8 kcal/mol higher in energy than the planar geometry.

Various properties of triplet states of hexatrienes have been investigated experimentally. From singlet-triplet absorption spectra in methylene iodide the vertical triplet energy has been found to be 2.03 eV for (E)-1,3,5-hexatriene,¹⁸ 2.07 eV for (Z)-1,3,5-hexatriene,¹⁸ and 2.04 eV for neoalloocimene.¹⁹ The energies of the two lowest triplet states of 1,3,5-hexatriene in the gas phase have also been determined by electron energy loss measurements [ref 20 and references therein]. Theoretical results locate the T_1 state of the E isomer at 2.71 eV and T_2 at 4.32 eV.²¹ $T_n \leftarrow T_1$ absorption spectra have been obtained for neoalloocimene¹⁹ and (E,E)-1,3,5-heptatriene.²² Both spectra show an absorption maximum around 315 nm in the difference absorption spectra. The triplet lifetime has been determined to be 333 ns for neoalloocimene¹⁹ and 294 ns for (E,E)-1,3,5-heptatriene.²²

The singlet-state photochemistry of hexatrienes generally involves relatively efficient, reversible interconversions of the E and Z isomers and the corresponding 1,3-cyclohexadienes. Further products are formed from each of these isomers. The importance of the ground-state conformation in controlling these photo-reactions was expressed in the principle of nonequilibration of excited rotamers (NEER).²³ The composition of the ground-state equilibrium of rotamers is different for hexatrienes methylated at different positions. For the central-Z isomers of 1,3,5-hexatriene, 2-methyl-1,3,5-hexatriene, and 2,5-dimethyl-1,3,5-hexatriene the equilibrium is shifted from predominantly tZt via cZt to cZc.^{23,24} The composition of the photoproduct mixture from each of these compounds will reflect the shift in the conformational equilibrium if the various rotamers, upon excitation, transform into different excited species that do not equilibrate but yield their own specific photoproduct(s).

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An alternative explanation of conformational control of photochemistry²⁵ would involve rotameric interconversion in the excited state to an equilibrium of conformers similar to the ground-state equilibrium; it requires the additional assumption that comparable steric effects are operative in the excited and the ground states. This explanation could be discarded after a study of the wavelength dependence of the photoreactions of (*E*)-2,5-dimethyl-1,3,5-hexatriene (*E*-DMH) and (*Z*)-2,5-dimethyl-1,3,5-hexatriene (*Z*-DMH).^{23,26}

Upon irradiation of *Z*-DMH the coexistence of *cZc* and *cZt* conformers with different absorption characteristics leads to a mixture of excited rotamers, the composition of which is wavelength-dependent. If interconversion between rotamers is rapid, as compared to the rate of decay to the products, the photoproduct mixture will *not* reflect the wavelength-dependent population of the excited state. Experimentally it was found that *Z*-DMH irradiated at 313 nm produces 1,4-dimethyl-1,3-cyclohexadiene and *E*-DMH in a 6:1 ratio. At 254 nm the ratio is reversed, *Z*-*E* isomerization being 10 times more effective. Irradiation of *E*-DMH gives mainly *Z*-DMH at both wavelengths.

The short lifetimes of excited singlet states are among the arguments given in support of the NEER principle. This argument is less valid in the case of triplet excited states. However, a comparable line of thought is followed in the interpretation of triplet sensitized photoisomerization of butadienes.^{23,27} Moreover, it should be noted that the product distributions from sensitized and direct photoisomerization of hexatrienes are different, with *E*-*Z* isomerization being more efficient from the triplet state as seen from the biacetyl-sensitized photochemistry of 1,3,5-hexatriene.^{23,28}

The isomeric distribution upon sensitized photoisomerization of the four *E*-*Z* isomers of 2,6-dimethyl-2,4,6-octatriene has been investigated by Butt et al.⁴ using benzophenone as sensitizer with irradiation at 366 nm. Without quencher the photostationary state distribution was ca. 35% of the *E,E* isomer, ca. 25% of the *E,Z* isomer, and ca. 20% of each of the two central-*Z* isomers. The individual quantum yields of triplet isomerization were also reported. The values were all comparatively high (0.15 or higher), even for the interconversions between the central-*E* and the corresponding sterically hindered central-*Z* isomers. With high levels of an azulene quencher only small amounts of the central-*Z* isomers were present in the photostationary state. These authors conclude that in the excited state a planar central-*E* geometry is much more stable than a planar central-*Z* geometry and that the former is in equilibrium with a geometry that is twisted around the central double bond. The twisted geometry has an energy between those of the two planar geometries and is separated from the planar central-*E* isomer by an energy barrier.

Generation of triplet states by flash photolysis has been reported for various dienes,²⁹ using acetone as sensitizer and acetonitrile as solvent.

Ground-state vibrational spectra have long been known for (*E*)- and (*Z*)-1,3,5-hexatriene.^{30,31} Myers et al.³² have reported a preresonance Raman spectrum of (*E*)-1,3,5-hexatriene, excited

at 299.1 nm. After some controversies³⁰⁻⁴⁰ it can now be regarded as well established to assign the band at 1187 cm⁻¹ in (*E*)-1,3,5-hexatriene to the C-C single bond stretching mode.³⁴

Excited singlet states of hexatriene cannot be studied by emission-detected excitation spectroscopy, since no emission has been observed from 1,3,5-hexatriene.^{33,41,42} Leopold et al.³⁹ have obtained electronic absorption spectra of (*E*)-1,3,5-hexatriene in a supersonic jet expansion. In the excited ¹B_u⁺ state they observe vibronic progressions involving 1631-, 1224-, 718-, and 313-cm⁻¹ vibrations. The 1631-cm⁻¹ mode is assigned to the in-phase C=C double bond stretching mode, whereas the 1224-cm⁻¹ mode is assigned to the C-C single bond stretching mode.

Vibrations in the excited triplet states of polyenes have been studied by the time-resolved resonance Raman technique developed initially in our laboratory.^{43,44} With this technique we have studied β -carotene,^{7,8} retinal,^{11,45} and diphenylbutadiene.⁴⁶ Recently we reported transient Raman spectra of the lowest excited triplet states of short, olefinic polyenes: (*E*)-1,3,5-hexatriene,⁴⁷ (*E,E*)-1,3,5-heptatriene,²² (*E,E,E*)-2,4,6-octatriene,⁴⁸ and the (*E,E*)-alloocimene and (*E,Z*)-neoalloocimene isomers of 2,6-dimethyl-2,4,6-octatriene.⁴⁸ To understand the structure of the lowest triplet states of these trienes, through an assignment of their transient resonance Raman spectra, (*E*)-2,5-dimethyl-1,3,5-hexatriene is an obvious extension of the study, because the position of the methyl groups is different from that in the hexatrienes studied hitherto. Furthermore, the existence of two different predominant ground-state conformers, *tEt* for *E*-DMH and *cZc* for *Z*-DMH, might give information regarding the validity of the NEER principle for the excited triplet states.

In this paper we report the UV absorption and Raman spectra of the ground states and the time-resolved resonance Raman spectra of the lowest triplet states of the *E* and *Z* isomers of 2,5-dimethyl-1,3,5-hexatriene. The triplet states were created by sensitized laser flash photolysis, and their vibrational structure were investigated by time-resolved resonance Raman spectroscopy using a pump-probe technique with two pulsed lasers.

Experimental Section

Materials. Acetonitrile (Merck, LiChrosolv), methanol (Ferak, p.a.), acetone (Ferak, p.a.), and isooctane (Merck, Uvasol) were used as received. The synthesis and separation of (*E*)- and (*Z*)-2,5-dimethyl-1,3,5-hexatriene have been described previously.^{49,50} The purified samples were put in glass capillaries under nitrogen, and the capillaries were cooled briefly and sealed.

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Throughout the transient experiments the capillaries with the 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 ~ 35 min.

Methods. Ground-state UV absorption measurements were performed on a Cary 219 spectrometer. The experimental setup for transient Raman experiments in combination with pulse radiolysis has been described previously.⁵¹ However, as the instrumentation has been changed continuously since then and adapted to laser flash photolysis,^{22,48,52} a detailed description will be given here. The transient species were created and detected in a pump-probe arrangement with two pulsed lasers, both pulsed at a rate of 5 Hz. An excimer laser (Lambda Physics EMG 102E) emitting at 308 nm (XeCl) with pulses of 13-ns duration and an energy of 10 mJ/pulse was used as pump source. The probe laser for exciting the transient resonance Raman spectra was a Nd:YAG pumped dye laser (Quantel). A wavelength of 315 nm was obtained by frequency doubling the output of DCM laser dye at 630 nm pumped by the second harmonic of the Nd:YAG at 533 nm. In this way pulses of 10-ns duration and an energy which varied from 2.5 to 3 mJ were obtained.

The dye laser pulses could be delayed in time with respect to the excimer laser, the delay being monitored with a vacuum photodiode (Instrument Technology TF 1850). The relative jitter between the two laser pulses was less than 10 ns. The sample cell was cylindrical, 26 mm inner diameter, 6 mm inner height, and was spinning during the experiments. The two laser beams were brought together nearly collinearly from above on the sample cell. The pump and probe beams were weakly focused on the top of the cell, the former to an area of 1.3×0.6 mm, the latter to an area of 1.0×0.3 mm, resulting in pump and probe intensities of ~ 100 MW cm⁻². The overlap between the two laser beams was optimized for maximum transient absorption. Each Raman spectrum was averaged over 50 or 100 laser pulses, this number being limited by the total amount of sample available and the photoisomerization occurring upon laser irradiation, as discussed below. The scattered Raman light was collected through a computer-optimized Suprasil lens system in the horizontal plane of the cell, and imaged on to a home-built Czerny-Turner single monochromator with a focal length of 600 mm and a holographic grating of 2400 grooves/mm. The dispersed light from the monochromator was intensified by a gated (30 ns) image intensifier (Varo 5772) and detected by an optical multichannel analyzer (SIT-vidicon TV camera), coupled fiber-optically to the image intensifier. The vidicon camera has been described in detail previously.⁵¹ The distribution of scattered light along the direction of the two laser beams over the height of the cell was observed throughout the experiments by viewing the real-time TV image from the vidicon. The integration limits⁵¹ were adjusted such that only the scattered light from the upper 3 mm of the cell, where the concentration of transient species was highest due to the attenuation of the pump laser beam by absorption from the sensitizer, was detected. In the region 800–1800 cm⁻¹, the 290 channels of the vidicon covered ~ 917 cm⁻¹, corresponding to a dispersion of ~ 3 cm⁻¹/channel. The spectral resolution determined by the used slit width (0.2 mm) of the monochromator was ~ 12 cm⁻¹. The optical multichannel analyzer was coupled via a CAMAC ADC (12 bits) to a PDP 11/23 computer where the collection, averaging, display, and handling of data took place.

Raman spectra were calibrated by using known bands from a mixture of cyclohexane and *p*-xylene (3:1, v/v). In this procedure a second-order polynomial for the dependence of wavelength upon channel number was assumed and fitted to the experimental band positions of the solvent mixture by nonlinear regression. The absolute limits of error of this method, as estimated from the deviation of calculated wavenumbers from literature values, were

Figure 1. Ground-state UV absorption spectra of 4.74×10^{-5} M *E*-DMH in isooctane (broken line) and 7.70×10^{-5} M *Z*-DMH in isooctane (full line).

± 2 cm⁻¹ for strong Raman bands. The system was recalibrated several times a day because of a weak temperature dependence of the vidicon. All spectra shown are the ones resulting after subtraction of the base line obtained with no light on the detector. No other corrections not mentioned in the paper were performed.

When spectra obtained with different calibrations were added and subtracted, channel numbers for one spectrum were converted to wavenumbers, which were again converted to decimal channel numbers for the other spectrum. Pairs of channels for which the channel in the other spectrum was the closest to the decimal channel number calculated from the first spectrum were then used to combine the spectra.

For capillary gas chromatography an SGE flexible fused-silica capillary column (25 m long, 0.25 mm diameter) with the chemical-bonded CP Sil 5 CB/BP0 phase corresponding to an OV-1 phase was installed in a Hewlett-Packard 5730A gas chromatograph equipped with a split system (1:100) in connection with the injection port (200 °C). Column temperature was 60 °C, detector (FID) 200 °C, and flow rate 1 mL of N₂/min.

Results

Ground-State Spectra. Ground-state UV absorption spectra of 4.74×10^{-5} M (*E*)-2,5-dimethyl-1,3,5-hexatriene and 7.70×10^{-5} M (*Z*)-2,5-dimethyl-1,3,5-hexatriene in isooctane are shown in Figure 1. Wavelengths and extinction coefficients of absorption maxima of *E*-DMH and *Z*-DMH are listed in Table I together with literature values for 1,3-butadiene, (*Z*)-hexatriene, (*E*)-hexatriene, and (*E,E,E*)-octatriene. There are several characteristic differences between the spectra of the two isomers. The extinction coefficients are larger for *E*-DMH than for *Z*-DMH and the spectrum of *Z*-DMH is blue-shifted compared to that of *E*-DMH. The spectrum of *Z*-DMH is less structured than that of *E*-DMH, and the *Z*-DMH spectrum shows only two peaks, whereas the *E*-DMH spectrum shows three peaks and two shoulders.

Ground-state Raman spectra excited at 514.5 nm and recorded with a conventional scanning Raman spectrometer⁵⁴ and ground-state FTIR absorption spectra were obtained of neat samples of *E*-DMH and *Z*-DMH. These spectra will be reported elsewhere⁵⁵ and shall only be mentioned briefly here. The Raman

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TABLE I: Wavelengths and Extinction Coefficients of UV Absorption Maxima of 1,3-Butadiene, (Z)-2,5-Dimethyl-1,3,5-hexatriene, (E)-2,5-Dimethyl-1,3,5-hexatriene, (Z)-1,3,5-Hexatriene, (E)-1,3,5-Hexatriene, and (E,E,E)-2,4,6-Octatriene

compound	wavelength, nm	extinction coeff, M ⁻¹ cm ⁻¹
butadiene ^{a,b}	204	20 900
	209	24 400
	216	17 400
(Z)-dimethylhexatriene ^{c,d}	207	9 800
	237	12 500
(E)-dimethylhexatriene ^{d,e}	250	31 600
	259	43 000
	270	33 800
(Z)-hexatriene ^{f,g}	247	30 700
	256	41 100
	267	31 200
(E)-hexatriene ^{f,g}	248	35 700
	257	51 900
	267	42 500
(E,E,E)-octatriene ^{h,i}	253	31 000
	263	55 000
	274	44 400

^a Vapor phase, 9.8 mmHg, 25 °C. ^b Reference 53. ^c In isooctane, 7.70×10^{-5} M. ^d This work. ^e In isooctane, 4.74×10^{-5} M. ^f In *n*-heptane. ^g Reference 18. ^h In heptane. ⁱ Reference 25.

spectra were clearly different for the two isomers. *E*-DMH shows strong bands at 1624, 1295, and 1032 cm⁻¹, with no observable bands between the latter two wavenumbers. *Z*-DMH shows strong bands at 1630, 1312, and 967 cm⁻¹. For this isomer the only observable band in the region 1050–1300 cm⁻¹ is a weak one at 1214 cm⁻¹. The overall intensity is stronger for *E*-DMH than for *Z*-DMH. The *E*-DMH band at 1624 cm⁻¹ is 9 times stronger than the *Z*-DMH band at 1630 cm⁻¹. However, the band width of the latter is 3 times larger, so the integrated intensities of these bands differ only by a factor 3 between the two isomers.

Transient Raman Spectra. Transient Raman spectra, excited at 315 nm, of Ar-saturated solutions of 0.012 M (*E*)-2,5-dimethyl-1,3,5-hexatriene in acetonitrile with 0.54 M acetone as sensitizer are shown in Figure 2A–D, and of 0.012 M (*Z*)-2,5-dimethyl-1,3,5-hexatriene in acetonitrile with 0.54 M acetone in Figure 2A'–D'. Spectra are shown for the region 800–1800 cm⁻¹. The region 200–1200 cm⁻¹ was investigated as well, but no transient bands were found. It should be noted that the intensity scales differ for the individual spectra in Figure 2. These scales are indicated in the figure caption and should be taken into account when comparing relative intensities. In the recording of the spectra underlying Figures 2 and 3 each sample was used for recording a ground-state Raman spectrum of the sample before laser flash photolysis, a transient Raman spectrum, an additional transient Raman spectrum, and finally a ground-state Raman spectrum of the sample after laser flash photolysis. For some samples each spectrum was averaged over 100 pulses, for other samples over 50 pulses. Consequently, recording of the spectra mentioned above corresponds to each sample being exposed to a series of 100 (50) probe-only pulses, followed by 100 (50) pump-and-probe pulses, additional 100 (50) pump-and-probe pulses, and finally 100 (50) probe-only pulses. The spectra in Figure 2, A and A', were obtained with probe pulses only. Figure 2A shows the strong ground-state Raman bands of *E*-DMH at 1624, 1295, and 1032 cm⁻¹ mentioned above. Acetonitrile bands are seen at 1372 cm⁻¹, extending to 1500 cm⁻¹, and at 917 cm⁻¹. Acetone has strong bands at 1712, 1428, 1220, and 1065 cm⁻¹; these are barely seen in the spectrum. Figure 2A' shows the bands from acetonitrile and acetone, plus a weak band at 1040 cm⁻¹ from acetonitrile. As noted above, the ground-state Raman spectrum of *Z*-DMH is weaker than that of *E*-DMH. In Figure 2A' only the band at 1630 cm⁻¹ is seen clearly. Even the bands at 1312 and 967 cm⁻¹ can barely be seen in the spectrum. The spectra in Figure 2, B

Figure 2. Time-resolved resonance Raman spectra of (A–D) 0.012 M *E*-DMH, 0.54 M acetone in acetonitrile and (A'–D') 0.012 M *Z*-DMH, 0.54 M acetone in acetonitrile. Pump wavelength 308 nm, probe wavelength 315 nm. (A and A') Probe pulse only; (B) at 60 ns and (B') at 80 ns delay between pump and probe pulses; (C) spectrum B – 0.15 × spectrum A; (C') spectrum B' – 0.135 × spectrum A'; (D and D') probe pulse only. Obtained by subtraction of spectra taken before and after irradiation with pump pulses. Intensities expanded by (A–D) and (A'–D'): 1, 8, 32, ~8, respectively. Solvent denoted by S, sensitizer by S', ground-state bands from *E*-DMH and *Z*-DMH by *G_E* and *G_Z*, respectively, and triplet bands by T.

and B', were obtained with time delays between the pump and probe pulses of 60 and 80 ns, respectively. Ground-state bands from solvent, sensitizer, and trienes are seen with decreased intensity due to transient absorption of both the exciting light and the scattered Raman light. In addition transient Raman bands are seen around 1550 and 1150 cm⁻¹ for both isomers, together with a weak shoulder around 1350 cm⁻¹ on the strong acetonitrile 1372-cm⁻¹ band. Figure 2C represents subtraction of the spectrum in Figure 2A from the spectrum in Figure 2B after rescaling of spectrum 2A such that the acetonitrile band at 1372 cm⁻¹ disappears after subtraction. Figure 2C' represents subtraction of the spectrum in Figure 2A' from the spectrum in Figure 2B', again after rescaling of spectrum 2A'. Both parts C and C' of Figure 2 clearly show the transient bands around 1550 and 1150 cm⁻¹. Several features appear in Figure 2C, C' which are not observed in Figure 2B, B'. In Figure 2C negative bands show up around 1625, 1300, and 1035 cm⁻¹. Positive bands appear in Figure 2C' around the same wavenumbers. A negative band is seen around 917 cm⁻¹ in both parts C and C' of Figure 2. A number of weak bands can be observed in the region 1350–1400 cm⁻¹, around 1390 and 1360 cm⁻¹ for *E*-DMH, and around 1350 cm⁻¹ for *Z*-DMH. Additional weak bands may be seen around 1390 and 1250 cm⁻¹ for the *Z* isomer. Figure 2D represents subtraction of a probe-only spectrum, taken before irradiation with pump pulses of a sample of the *E* isomer, from a probe-only spectrum taken after irradiation of the sample with pump pulses in the transient experiments. Figure 2D shows three negative bands, around 1625, 1300, and 1035 cm⁻¹, corresponding to similar features in Figure 2C. Figure 2D' represents subtraction of probe-only spectra for the *Z* isomer, and shows positive peaks around 1625, 1300 and 1035 cm⁻¹, corresponding to similar features in Figure 2C'.

Around the wavenumbers of the strong solvent bands, 1372 cm⁻¹ and upwards, and 917 cm⁻¹, bands are seen in both parts D and D' of Figure 2 that are weak compared to their counterparts in Figure 2A, A', respectively. We regard these features as artifacts arising from the subtraction of strong bands from each other. The weak bands in the region 1350–1400 cm⁻¹ are situated around the strong acetonitrile band at 1372 cm⁻¹. To examine whether these bands are real or artifacts due to the subtraction procedure in connection with the strong solvent band, a number of experiments were carried out with methanol as solvent. These experiments confirmed the bands around 1390 and 1360 cm⁻¹ for *E*-DMH and the band around 1350 cm⁻¹ for *Z*-DMH, whereas the band around 1390 cm⁻¹ could not be confirmed for the *Z* isomer.

Figure 3. Time-resolved resonance Raman spectra of (A) 0.012 M *E*-DMH, 0.54 M acetone in acetonitrile and (B) 0.012 M *Z*-DMH, 0.54 M acetone in acetonitrile. Pump wavelength 308 nm, probe wavelength 315 nm. (A) Summation of eight subtraction spectra with delays varying from 60 to 80 ns. (B) Summation of eight subtraction spectra with delays varying from 50 to 130 ns.

An interpretation of the kind of spectra presented in this paper involves evaluation of detailed features. The exact position of the two strongest transient Raman bands of *E*-DMH and *Z*-DMH varied from experiment to experiment by less than ± 2 cm^{-1} . As this variation is due to a limited signal-to-noise ratio a number of individual sets of experiments like the ones in Figure 2A–D and 2A'–D' were carried out and averaged. Subtraction spectra like the one in Figure 2C were averaged over eight sets of experiments, and a region from the resulting averaged spectrum is shown in Figure 3A for the *E* isomer. The same procedure yielded spectrum 3B for the *Z* isomer. No changes in frequencies or relative intensities of the 1550- and 1150- cm^{-1} bands were observed for spectra obtained with delays in the region 50–130 ns. Hence, averaging of spectra with delays from 50 to 130 ns as used in the generation of Figure 3 is justified. We did not observe changes in frequencies and relative intensities at longer delays, but with the lower intensity and signal-to-noise ratio of the transient bands the uncertainty is larger in this case. Figure 3A,B confirms the bands mentioned above on the basis of Figure 2C,C'. However, the bands around 1390 and 1250 cm^{-1} for the *Z* isomer still appear doubtful in Figure 3B.

The wavenumbers found for the strong transient band around 1550 cm^{-1} may be influenced by the proximity of the ground-state band around 1625 cm^{-1} . The same argument should not apply to the transient band around 1150 cm^{-1} , since this band is found in a region without detectable ground-state bands from either *E*-DMH, *Z*-DMH, 1,4-dimethyl-1,3-cyclohexadiene, acetonitrile, or acetone, as seen from Figure 2. A comparison was made of the position of the 1550- and 1150- cm^{-1} bands in pump-and-probe spectra like Figure 2B,B' and in subtraction spectra like Figure 2C,C'. For the eight sets of spectra for each isomer the 1150- cm^{-1} band showed no deviations. The 1550- cm^{-1} band showed no deviation for the *Z* isomer, whereas for the *E* isomer the eight sets of spectra showed a deviation ranging from 1 to 1.5 cm^{-1} , the wavenumbers found from the subtraction spectra being from 1 to 1.5 cm^{-1} higher than the ones found from the pump-and-probe spectra. This deviation should be kept in mind in the evaluation of the wavenumbers of the transient bands.

A final point should be made in connection with the determination of the exact position of bands in the transient spectra. As mentioned above the calibration from channel numbers to wavenumbers was carried out by using a solution of *p*-xylene in cyclohexane. However, an independent measure of the wavenumber accuracy is found in the positions of strong ground-state bands of solvent and trienes. The values for the solvent bands can be compared to literature values, and the values for triene ground-state bands to the values found in the spectra obtained from neat samples with the scanning Raman spectrometer mentioned above.

In the above we have stated approximate wavenumbers for various bands in the transient spectra. Evaluation of the position in the mentioned eight sets of experiments for each isomer of transient bands, ground-state double bond stretching bands, and the two strong acetonitrile bands gave mean and standard deviation

TABLE II: Observed Ground-State Raman Bands (cm^{-1}) of Acetonitrile, Ground-State Raman Bands of (*E*)- and (*Z*)-2,5-Dimethyl-1,3,5-hexatriene, and Transient Raman Bands of the Lowest Excited Triplet States of (*E*)- and (*Z*)-2,5-Dimethyl-1,3,5-hexatriene in Time-Resolved Resonance Raman Spectra^c

	(<i>E</i>)-dimethylhexatriene	(<i>Z</i>)-dimethylhexatriene
triene ground-state band	1625.0 (0.2) ^a	1629.1 (1.7) ^b
triene transient band	1551.3 (1.5) ^c	1547.6 (0.8) ^c
triene transient band	1388.6 (1.6) ^c	1391.8 (2.4) ^{c,d}
acetonitrile	1374.4 (0.1) ^a	1374.4 (0.4) ^a
triene transient band	1356.8 (3.1) ^c	1350.4 (1.4) ^c
triene transient band	1146.1 (0.9) ^c	1151.3 (1.1) ^c
acetonitrile	917.7 (0.4) ^a	918.0 (1.4) ^a

^a From pump-and-probe spectra. ^b From probe-only spectra. ^c From subtraction spectra. ^d Doubtful. ^e Mean values from eight sets of experiments; standard deviations are given in parentheses.

for the position of each of these bands. These are listed in Table II. The wavenumbers listed for transient bands correspond to values found in subtraction spectra and those for ground-state bands in pump-and-probe spectra or probe-only spectra.

Gas Chromatography. To examine the purity of the samples and the photochemical conversion of the isomers in connection with the creation of excited species, all samples were analyzed by GC before and after laser flash photolysis. The initial purity of the samples before irradiation varied from 98% to 99%. No differences were found between spectra obtained from samples with initial purity 98% or 99% in one isomer.

The analysis of samples after laser flash photolysis was complicated by the fact that on the column used base-line separation was not obtained between (*E*)-2,5-dimethyl-1,3,5-hexatriene and a compound which on the basis of its retention time was identified as 1,4-dimethyl-1,3-cyclohexadiene. Dimethylcyclohexadiene was seen as a weak shoulder with shorter retention time on the (*E*)-dimethylhexatriene peak at slightly above 6 min retention time. (*Z*)-Dimethylhexatriene showed a retention time close to 4 min. However, a qualitative assessment of the presence of dimethylcyclohexadiene could be obtained. The conditions of the laser flash photolysis experiments did not create any products detectable by GC other than conversion between *E*-DMH, *Z*-DMH, and dimethylcyclohexadiene.

Chromatograms of solutions of the *Z* isomer after the cell had been exposed to 200 probe-only pulses and 200 pump-and-probe pulses showed that the *Z* isomer had decreased to 93%, whereas the combined amount of the *E* isomer and dimethylcyclohexadiene had grown to 6%, with the former being the dominant one. After a total of 300 probe-only pulses and 300 pump-and-probe pulses the corresponding numbers were 90% and 9%. Chromatograms of solutions of the *E* isomer that had been exposed to 200 probe-only pulses and 200 pump-and-probe pulses showed that the *Z* isomer had grown to 5%, whereas after 300 probe-only and 300 pump-and-probe pulses the *Z* isomer had grown to 9%. In addition a small contribution from dimethylcyclohexadiene could be seen as a weak shoulder on the peak representing the *E* isomer. Samples of (*E*)- and (*Z*)-dimethylhexatriene in acetonitrile without the acetone sensitizer were analyzed by GC after exposure to 400 probe-only pulses and 200 pump-and-probe pulses. For the *Z* isomer a combined yield of 3% of the *E* isomer and dimethylcyclohexadiene was found, with the latter as the dominant species. For the *E* isomer the chromatograms showed a yield of the *Z* isomer in the order of 0.2%, with a weak shoulder on the (*E*)-dimethylhexatriene peak representing dimethylcyclohexadiene.

Kinetics. In the pump-and-probe spectra the intensity is decreased by absorption from the transient species of the exciting probe laser light and of the scattered Raman light. This influence on the intensity of Raman bands of the transient absorption takes place in a complex way.^{46,56} Besides, the kind of transient ex-

Figure 4. Logarithmic plots of the intensity of the transient 1551/1548-cm⁻¹ band relative to the intensity of the solvent 1372-cm⁻¹ band for (A) 0.012 M *E*-DMH, (A') 0.012 M *Z*-DMH, and (A'') 0.003 M *Z*-DMH for different delays between pump and probe laser pulses. I_{1550} corresponds to I_{1551} for *E*-DMH and I_{1548} for *Z*-DMH.

periments that we present in this paper are carried out in the frequency domain and are not ideal for determining kinetics of reactions. Kinetics are better determined by transient absorption experiments carried out in the time domain for fixed wavelengths. Two methods exist, however, with which one can obtain a measure of the transient lifetime from Raman intensities.⁵⁶ Applied to the present experiments the first method consists in monitoring the intensity of the 1372- and 917-cm⁻¹ solvent bands for different time delays between the pump and probe lasers and the second in measuring the intensity of the transient band around 1550 cm⁻¹ relative to the intensity of the 1372-cm⁻¹ solvent band for different time delays. As the latter method involves fewer assumptions we will use this one in the following.

Assuming triplet energy transfer from acetone to the trienes and first-order decay of triene triplets, the concentration of the triene in the triplet state can be described by⁵⁷

$$[\text{triene}^T] = \{[A^T]k_{ET}[\text{triene}]/(k_1 - k_{ET}[\text{triene}])\} \times \{\exp(-k_{ET}[\text{triene}]t) - \exp(-k_1t)\}$$

where t is the time delay between the pump and probe laser pulses. $[A^T]$ is the concentration of acetone triplets. The buildup of these follows the laser pulse,⁵⁸ and their rate of self-decay is assumed to be much smaller than the rate of energy transfer to trienes. The initial concentration of triene, $[\text{triene}]$, is 0.012 M, and k_{ET} is the rate constant for energy transfer from the acetone sensitizer triplet to triene. This rate constant has been found to be $\sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for triplet energy transfer from acetone to various dienes in acetonitrile.²⁹ The triplet state of acetone has a lifetime of 47 μs in acetonitrile,⁵⁹ corresponding to a rate of self-decay of $2.1 \times 10^4 \text{ s}^{-1}$. This is seen to be much smaller than the rate of energy transfer to trienes, $k_{ET}[\text{triene}]$, which is determined from the values above to be $4.8 \times 10^7 \text{ s}^{-1}$. k_1 is the rate constant for first-order decay of the triene triplet. From measurements of transient differential absorption following pulse radiolysis it has been found to be $3.0 \times 10^6 \text{ s}^{-1}$ for neoalloocimene in toluene¹⁹ and $3.4 \times 10^6 \text{ s}^{-1}$ for 1,3,5-heptatriene in toluene.²² For $t = 50 \text{ ns}$ $\exp(-k_1t)$ is ~ 10 times larger than $\exp(-k_{ET}[\text{triene}]t)$. Hence, a plot of $\ln [\text{triene}^T]$ as a function of t should be linear with slope $-k_1$ for t larger than 50 ns.

Under the assumptions mentioned below the ratio of the intensity of the transient band around 1550 cm⁻¹ to the intensity of the solvent band at 1372 cm⁻¹ is independent of the amount of transient absorption and a direct measure of the relative concentration of triene triplets. As the concentration of acetonitrile is constant, a plot of $\ln (I_{1550}(t)/I_{1372}(t))$ as a function of the time delay between the pump and probe laser pulses should then be

linear with slope $-k_1$. A plot of $\ln (I_{1550}(t)/I_{1372}(t))$ is shown in Figure 4A for the *E* isomer and in Figure 4A' for the *Z* isomer. To investigate the possible quenching of triplet molecules by ground-state trienes, we repeated the measurements with a lower concentration (0.003 M) of the *Z* isomer. Figure 4A'' shows a plot of $\ln (I_{1550}(t)/I_{1372}(t))$ for this concentration. In the recording of the spectra underlying Figure 4 each sample was exposed to 100 probe-only pulses, followed by up to eight sets of 50 pump-and-probe pulses, and finally 100 probe-only pulses.

It should be mentioned that two assumptions are involved in the method used: (i) the transient absorption is due to triene triplets alone, and (ii) these triplets are distributed homogeneously over the solution. We see no indication of transient absorption from other species than triene triplets. Hence, we consider assumption i to be justified. However, transient species are created only in the part of the cell that is exposed to the pump laser beam, and within this volume the concentration of transient species decreases along the direction of the pump laser beam. From this it is clear that assumption ii is only partly justified.

Straight lines fit reasonably well with curves 4A, 4A', and 4A'', up to a delay of 300 ns, and show a k_1 of $12.7 \times 10^6 \text{ s}^{-1}$ for 0.012 M *E*-DMH, a k_1 of $9.4 \times 10^6 \text{ s}^{-1}$ for 0.012 M *Z*-DMH, and a k_1 of $6.0 \times 10^6 \text{ s}^{-1}$ for 0.003 M *Z*-DMH, corresponding to triplet lifetimes of 79, 106, and 168 ns.

Discussion

Traetteberg and Paulen have studied the molecular structure of the ground states of the *E* and *Z* isomers of 1,3,5-hexatriene⁶⁰ and 2-methyl-1,3,5-hexatriene⁶¹ by the gas electron diffraction method. These authors found that the *E* isomers of both compounds in the vapor phase have essentially planar carbon skeletons with *s*-trans conformation at the C-C single bonds. For the *Z* isomer of 1,3,5-hexatriene considerable steric strain resulted in a torsional angle of 10° around the central C=C double bond, while for the *Z* isomer of 2-methyl-1,3,5-hexatriene the C₃=C₄ and C₅=C₆ double bonds were found to be coplanar, with *s*-trans conformation around the C₄-C₅ single bond and with the C₁=C₂ double bond being out of the plane of the other C=C double bonds.

We do not expect the additional methyl group on C₅ to destroy the planarity of the carbon skeleton in the *E* isomer. In the *Z* isomer, however, methyl substitution on both C₂ and C₅ is likely to induce even more steric hindrance than methyl substitution on C₂ alone, and the nonplanarity of the *Z* isomer should be even more pronounced for 2,5-dimethyl-1,3,5-hexatriene than for 2-methyl-1,3,5-hexatriene. As mentioned above the predominant conformers of the central-*Z* isomers of 1,3,5-hexatriene, 2-methyl-1,3,5-hexatriene, and 2,5-dimethyl-1,3,5-hexatriene probably are *tZt*, *cZt*, and *cZc*, respectively. Work is in progress on the conformations of various methylated hexatrienes using NMR.⁶²

Ground-State UV Absorption of (*E*)-Dimethylhexatriene. Wavelengths and extinction coefficients of absorption maxima are shown in Table I for 1,3-butadiene, (*Z*)-2,5-dimethyl-1,3,5-hexatriene, (*E*)-2,5-dimethyl-1,3,5-hexatriene, (*Z*)-1,3,5-hexatriene, (*E*)-1,3,5-hexatriene, and (*E,E,E*)-2,4,6-octatriene. From the above discussion on the basis of electron diffraction data the carbon skeletons of (*E*)-hexatriene, (*E*)-dimethylhexatriene, and (*E,E,E*)-octatriene are expected to be planar. Accordingly, the overall shape of the spectra of these three compounds and their extinction coefficients are quite similar. There are, however, differences between the three compounds in the wavelengths of the absorption maxima. The absorption maxima of *E*-DMH are red-shifted 2–3 nm from those of (*E*)-hexatriene, whereas the absorption maxima of (*E,E,E*)-octatriene are red-shifted 5–7 nm. This can be taken as an indication that 1,6-dimethylation is a larger perturbation of the $1^1B_u^+ \leftarrow 1^1A_g$ electronic transition in (*E*)-1,3,5-hexatriene than 2,5-dimethylation is.

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Ground-State UV Absorption of (Z)-Dimethylhexatriene. The UV absorption spectrum of (Z)-2,5-dimethyl-1,3,5-hexatriene is blue-shifted ~ 20 nm compared to (E)-2,5-dimethyl-1,3,5-hexatriene, and the maximum extinction coefficient of Z-DMH is less than $1/3$ of that of E-DMH. Whereas the peaks seen in the UV spectrum of E-DMH are due to vibronic progressions in the excited state, the two maxima in the less-structured Z-DMH spectrum probably are attributable to different electronic transitions. This is in agreement with the differences in molecular structure discussed above with extinction coefficients of ~ 10000 being typical for the cZc conformer.²⁵ A comparison of the similarity of the UV absorption spectra of (E)- and (Z)-hexatriene and the dissimilarity of those of (E)- and (Z)-dimethylhexatriene confirms the presence of steric hindrance with consequences for the molecular structure of Z-DMH.

In absorption spectra of jet-cooled octatetraene, hexatriene, and butadiene³⁹ wavelengths and extinction coefficients of the origins of absorption decrease, and vibronic bandwidths increase, with decreasing chain length. Three mechanisms are suggested to explain the increased vibronic bandwidths: unresolved vibronic excitations, vibronic coupling with a lower lying excited state, or very short excited-state lifetimes.³⁹ In a model calculation on excited states of 1,3-butadiene with geometries that are twisted around one of the double bonds, Dinur et al.⁶³ have shown how vibronic congestion of the electronic transitions can result in a spectral shape like the one of Z-DMH.

Similar differences in absorption spectra of the E and Z isomers are found for stilbene. In that case it was concluded that (Z)-stilbene twists more rapidly around the central double bond than (E)-stilbene.^{64,65} Hence, a comparison with stilbene suggests a more rapid twisting around the central C=C double bond for Z-DMH than for E-DMH in the S_1 state.

An additional explanation of the difference between the UV absorption spectra of E-DMH and Z-DMH is possible. Even though the cZc conformation is assumed to be dominant for Z-DMH, the exact conformer composition is unknown, and several conformers may contribute to the UV absorption spectrum of Z-DMH leading to a less structured spectrum.

Transient Experiments. The present experiments on (E)- and (Z)-dimethylhexatriene were performed with acetonitrile as solvent (methanol in a few cases) and acetone as sensitizer.^{22,29,47,48} Acetone was chosen as sensitizer because of its absorption at 308 nm, its high intersystem crossing efficiency, its weak absorption at 315 nm (wavelength of maximum $T_n \leftarrow T_1$ absorption of heptatriene and neoalloocimene), its triplet energy and lifetime, and the absence of any considerable fluorescence in the region 315–350 nm. The acetone concentration was adjusted to give an absorbance from acetone at 308 nm of ~ 2 per cm. The mechanism presumed to generate triene triplets is the following:

The excimer laser at 308 nm excites acetone in the singlet manifold. Via intersystem crossing⁶⁶ acetone converts to the triplet manifold. The triplet lifetime of acetone is 44–47 μ s in acetonitrile,⁵⁹ ~ 400 ns in methanol,⁶⁷ and the triplet energy 3.43–3.56 eV.⁶⁸ As mentioned above the vertical triplet energy of various trienes is slightly above 2 eV, so energy transfer from triplet acetone to trienes is exothermic, with subsequent population of the lowest triplet state of the trienes.

The $T_n \leftarrow T_1$ absorption spectra and triplet lifetimes of neoalloocimene¹⁹ and heptatriene²² are similar with absorption maxima at 315 nm and lifetimes of ~ 300 ns. We have assumed that the triplet absorption spectra and lifetimes of E-DMH and Z-DMH are close enough to those of neoalloocimene and heptatriene for the probe laser wavelength of 315 nm to be in resonance with $T_n \leftarrow T_1$ transitions of E-DMH and Z-DMH, and,

with delays between pump and probe laser pulses ranging from 50 ns to a few hundred nanoseconds as used in this study, for the dye laser to probe the lowest triplet states of E-DMH and Z-DMH, respectively.

No transient bands were seen in pump-and-probe spectra of solutions of acetone in acetonitrile, excluding the possibility that any transient bands are due to excitation of acetone only. Neither did samples of E-DMH or Z-DMH in acetonitrile or methanol without the acetone sensitizer show any transient bands, indicating that direct excitation of the trienes does not contribute to the transient Raman spectra. Furthermore, no transient bands are seen in Figure 2A,A', obtained on samples with acetone sensitizer but without the pump laser, which indicates that the transient species are generated by the pump laser.

Several types of reactions may interfere with the triplet energy transfer assumed to be responsible for the creation of the transient species. Singlet energy transfer from acetone to trienes can be neglected considering the endothermicity of this process. Another reaction possible is cycloaddition of singlet acetone to the trienes. The rate constant for cycloaddition of acetone to 2-methyl-2,4-hexadiene is $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.⁶⁹ With this rate constant and a maximum triene concentration of 0.012 M the pseudo-first-order rate constant of cycloaddition is $3.6 \times 10^6 \text{ s}^{-1}$, which is much lower than the rate constant of nonradiative decay of acetone singlets found to be $5.9 \times 10^8 \text{ s}^{-1}$.⁵⁸ Consequently, no significant quenching of the acetone excited singlet state is expected under the actual conditions.

Hydrogen abstraction by acetone triplets from the trienes must also be considered. In the present case quenching of triplet acetone by hydrogen or electron donors has rate constants of $(1-5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ as seen from the reaction of acetone with methyl- or ethyl-substituted ethylenes.⁶⁹ With the rate constant for triplet energy transfer from acetone to various dienes of $\sim 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ cited above, triplet energy transfer is seen to be much more efficient than this possible competing reaction.

Finally, hydrogen abstraction by triplet acetone from the solvent must be considered. This reaction would also lead to free radicals which might produce observable transients or influence the triene triplet states. Hydrogen abstraction by triplet acetone from acetonitrile can safely be excluded on the basis of the long intrinsic lifetime of triplet acetone in acetonitrile.⁵⁹ In methanol hydrogen abstraction from the solvent has a rate constant of $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ⁶⁷ resulting in a pseudo-first-order decay constant for triplet acetone of $2.5 \times 10^6 \text{ s}^{-1}$ in this solvent. Energy transfer to the trienes is however still faster, and at triene concentrations above 0.006 M more than 90% of the acetone triplet states will form triene triplets by energy transfer.

Together with the effect of oxygen on the lifetime of transient species generated from heptatriene,²² the above discussion supports the suggested mechanism involving triplet intermediates.

Transient Spectra. The GC analysis showed that the series of 200 probe-only pulses and 200 pump-and-probe pulses induce an isomeric conversion of $\sim 6\%$ in the bulk solutions. Consequently all spectra used in the construction of Figures 2 and 3 and Table II were obtained from samples with isomeric purity on the order of 93% or better. In Figure 2A,A' the position of solvent bands is in agreement with literature values, and the position of triene bands is in agreement with values obtained from the ground-state Raman spectra of neat samples, recorded with the scanning Raman spectrometer. Figure 2B,B' confirm that the probe laser wavelength is in resonance with the $T_n \leftarrow T_1$ transitions of both isomers, as seen from the attenuation of ground-state bands from solvent and trienes.

The purpose of the kind of subtraction spectra presented in Figure 2D,D' is to investigate possible buildup of stable products during the irradiation with laser pulses. These products include E-DMH, Z-DMH, and 1,4-dimethyl-1,3-cyclohexadiene. The UV absorption spectrum of 1,4-dimethyl-1,3-cyclohexadiene is known to have an absorption maximum at 265 nm with an ex-

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tion coefficient of $7770 \text{ M}^{-1} \text{ cm}^{-1}$.⁴⁹ Consequently, with excitation at 315 nm we expect dimethylcyclohexadiene to have a considerably weaker Raman spectrum than *E*-DMH. The C=C double bond stretch at 1576 cm^{-1} is by far the strongest Raman band of 1,3-cyclohexadiene,⁷⁰ and we do not expect this band to change much in going from cyclohexadiene to dimethylcyclohexadiene.

To investigate whether buildup of stable products had any effect on the transient spectra, subtraction spectra were constructed by subtraction from pump-and-probe spectra of probe-only spectra obtained from samples not only before (like in Figure 2C,C') but also after the pump-and-probe spectra. Furthermore, as pointed out previously⁴⁸ the concentration of products may be higher in the volume element that is exposed to pump-and-probe pulses, and where isomerization presumably takes place, than in the bulk solution. This possibility was investigated by subtraction of pump-and-probe spectra obtained with delays of 3–500 ns, that is, just after the decay of the transients but before products have diffused away from the irradiated volume, from pump-and-probe spectra with delays of 50–60 ns between laser pulses. These procedures did not reveal any new features other than the ones seen in Figure 2, and failed to show any bands in the vicinity of 1576 cm^{-1} , where the strong Raman band is expected for dimethylcyclohexadiene.

The GC analysis showed that conversion from the *E* to the *Z* isomer and from the *Z* to the *E* isomer takes place under the conditions of the laser flash photolysis experiments. Figure 2A,A' show that the overall intensity of the ground-state Raman spectrum of *E*-DMH is considerably stronger than that of *Z*-DMH. These facts together explain several of the features seen in Figure 2, C, C', D, and D'. The negative bands around 1625, 1300, and 1035 cm^{-1} in Figure 2C,D and the positive bands at corresponding wavenumbers in Figure 2C',D' are caused by the conversion between the isomers. However, in Figure 2C an additional contribution to the negative bands is the depletion of ground-state *E*-DMH in the volume irradiated by the pump laser. This explanation agrees with the assignment of several features in the transient spectra of 2,4,6-octatriene.⁴⁸ The amount of conversion between the isomers can be estimated from a comparison of the positive band around 1625 cm^{-1} in Figure 2D' and the negative band around 1625 cm^{-1} in Figure 2D to the band at 1625 cm^{-1} in Figure 2A. This estimate is in agreement with the amount of conversion found above from GC analysis.

The $T_n \leftarrow T_1$ absorption spectrum of heptatriene in toluene has a maximum at 315 nm, and the extinction coefficient falls to half the maximum value at 335 nm.²² In the transient Raman spectra with excitation at 315 nm, 800 cm^{-1} corresponds to 323 nm, and 1800 cm^{-1} to 334 nm. From this it is clear that with the present transient absorption low-wavenumber bands will appear weaker relative to high-wavenumber bands. If the probe-only spectrum is scaled to make the acetonitrile 1372-cm^{-1} band disappear in the subtraction from the pump-and-probe spectrum, bands at lower wavenumbers will be oversubtracted. This is what is observed in connection with the acetonitrile band at 917 cm^{-1} in Figure 2C,C'. In probe-only spectra no transient absorption is found, so scaling factors close to 1 are used in the construction of Figure 2D,D'. The weak bands at 917 cm^{-1} in Figure 2D,D' therefore do not have any significance.

The remaining bands, around 1550, 1390, 1360, and 1150 cm^{-1} for *E*-DMH and around 1550, 1390, 1350, 1250, and 1150 cm^{-1} for *Z*-DMH, are likely to belong to the lowest triplet states of the two isomers. In the spectra underlying Figure 4 the intensity of the bands around 1550 and 1150 cm^{-1} (data not shown) could be followed for both isomers as a function of the delay between the laser pulses. For each isomer the two bands disappeared at the same rate with rate constants as cited above, and no changes in frequencies were observed for spectra obtained with varying

delays. Hence, for each isomer the two bands are likely to belong to the same species. The exact position of the band around 1550 cm^{-1} for *E*-DMH is found from Table II and Figure 3A to be 1551 cm^{-1} with a standard deviation of 1.5 cm^{-1} . However, as mentioned above this position may be 1.5 cm^{-1} too high, because of the subtraction procedure in connection with the ground-state band around 1625 cm^{-1} . For *Z*-DMH the exact position of this band is found from Table II and Figure 3B to be 1548 cm^{-1} with a standard deviation of 1 cm^{-1} . However, because of the uncertainty in the position of the *E*-DMH 1551-cm^{-1} band, the observed difference of 3 cm^{-1} between *E*-DMH and *Z*-DMH is not sufficient to conclude firmly that the triplet spectra of the *E* and *Z* isomers are different.

Turning now to the second strong transient band observed, the exact position of the band around 1150 cm^{-1} is 1146 cm^{-1} for *E*-DMH, 1151 cm^{-1} for *Z*-DMH, with standard deviations of 1 cm^{-1} . As these positions from the subtraction spectra are unchanged from those of the corresponding pump-and-probe spectra it can be concluded that this band is placed at a higher wavenumber for *Z*-DMH than for *E*-DMH.

Although the spectrum of triplet *Z*-DMH in Figure 2B' was obtained with a delay of 80 ns compared to 60 ns for that of triplet *E*-DMH in Figure 2B, the 1548- and 1151-cm^{-1} bands in Figure 2B' are more intense compared to the 1372-cm^{-1} solvent band than the 1551- and 1146-cm^{-1} bands in Figure 2B. The same effect is observed in Figure 4, where the values on curve 4A' are less negative than the ones on curve 4A, reflecting that the transient 1550-cm^{-1} band is stronger relative to the solvent 1372-cm^{-1} band for *Z*-DMH than for the *E* isomer. This can be due either to a higher Raman scattering efficiency or to a higher concentration of triplet *Z*-DMH compared to *E*-DMH. The former reason is more likely because the rate of energy transfer from acetone to *Z*-DMH is probably not higher than to *E*-DMH.

The band around 1350 cm^{-1} is seen quite clearly as a shoulder on the 1372-cm^{-1} solvent band in Figure 2B' and the band around 1360 cm^{-1} less clearly as a shoulder in Figure 2B. The 1360-cm^{-1} band appears in Figures 2C and 3A and the 1350-cm^{-1} band in Figures 2C' and 3B, and both bands are confirmed in the experiments with methanol as solvent. Consequently, we regard both bands as real. From Figure 3 and Table II the exact positions are found to be 1357 cm^{-1} for *E*-DMH with a standard deviation of 3 cm^{-1} , and 1350 cm^{-1} for *Z*-DMH with a standard deviation of 1 cm^{-1} . For *E*-DMH a band appears around 1390 cm^{-1} in Figures 2C and 3A and is confirmed in the methanol experiments. The exact position is found to be 1389 cm^{-1} with a standard deviation of 2 cm^{-1} . For *Z*-DMH, bands around 1390 and 1250 cm^{-1} are seen weakly in Figures 2C' and 3B. However, these two bands are not confirmed in the methanol experiments and cannot be claimed to be real. *From the above it can be stated that the resonance Raman spectra of the lowest triplet states from the E and Z isomers of 2,5-dimethylhexatriene are different.* The $1551/1548\text{-cm}^{-1}$ band is probably at higher wavenumbers in *E*-DMH, the $1146/1151\text{-cm}^{-1}$ band is definitely at lower wavenumbers in *E*-DMH, the $1357/1350\text{-cm}^{-1}$ band is at higher wavenumbers in *E*-DMH, and a band corresponding to the *E*-DMH band at 1389 cm^{-1} probably is not found for *Z*-DMH. Moreover, the intrinsic Raman scattering efficiency of *Z*-DMH for the bands at 1548 and 1151 cm^{-1} probably is higher than that of *E*-DMH for the bands at 1551 and 1146 cm^{-1} . As their Raman spectra are different *the lowest triplet state from each of the two isomers (E)- and (Z)-2,5-dimethylhexatriene must have different geometries, or the two isomers must produce different mixtures of triplet species.*

Assignment of Transient Spectra. A detailed assignment of transient spectra of the type presented here is difficult at present due to the lack of theoretical calculations of band positions and intensities in excited triplet states and the lack of spectra from deuteriated or ^{13}C -substituted compounds. Moreover, the potential energy distributions in the vibrational normal modes of the excited state probably are considerably different from those in the ground state, which renders any direct correlation of spectra from ground and excited states doubtful. Nevertheless, a qualitative discussion

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TABLE III: Observed Transient Raman Bands (cm^{-1}) in Time-Resolved Resonance Raman Spectra of the Lowest Excited Triplet States of (*E*)-1,3,5-Hexatriene, (*E,E*)-1,3,5-Heptatriene, (*E,E,E*)-2,4,6-Octatriene, (*E*)-2,5-Dimethyl-1,3,5-hexatriene, and (*Z*)-2,5-Dimethyl-1,3,5-hexatriene

(<i>E</i>)- hexatriene ^a	(<i>E,E</i>)- heptatriene ^b	(<i>E,E,E</i>)- octatriene ^b	(<i>E</i>)-dimethyl- hexatriene	(<i>Z</i>)-dimethyl- hexatriene
1570	1567	1574	1551 1389 1357	1548 1392 ^c 1350
1270	1268	1264		
1234	1245	1252		
1200	1201	1205		
1106	1125	1136	1146	1151

^aReference 71. ^bReference 48. ^cDoubtful.

shall be attempted on the basis of a comparison with ground-state spectra and triplet spectra of other trienes. The positions of transient bands from (*E*)-hexatriene, (*E,E*)-heptatriene, (*E,E,E*)-octatriene, (*E*)-dimethylhexatriene, and (*Z*)-dimethylhexatriene are tabulated in Table III. For hexatriene, heptatriene, and octatriene we have assigned the strong transient band between 1500 and 1600 cm^{-1} to a C=C double bond stretching mode, shifted to lower wavenumbers in the triplet state. For an analogous assignment in 2,5-dimethyl-1,3,5-hexatriene the position of this band is significantly lower, and the shift from ground-state values (1624 cm^{-1} for *E*-DMH and 1630 cm^{-1} for *Z*-DMH⁵⁵) larger than for the other trienes mentioned. This could indicate that the change in geometry in going from the ground to the excited state is larger for 2,5-dimethyl-1,3,5-hexatriene than for hexatriene, heptatriene, and octatriene. Alternatively, the larger shift of the C=C stretching bands in *E*-DMH and *Z*-DMH compared to the other trienes might be a consequence of coupling of the lateral methyl groups with the adjacent C=C double bonds.

Turning now to the bands at 1146 cm^{-1} in *E*-DMH and 1151 cm^{-1} in *Z*-DMH we can compare with the corresponding spectra of hexatriene, heptatriene, and octatriene. Under the assumption that in these compounds the bands at 1106, 1125, and 1136 cm^{-1} , respectively, are due to the same vibrational mode, their position is apparently dependent on methylation. Their intensity is $\sim 30\%$ that of the strong bands around 1570 cm^{-1} . In contrast to these bands the position of the bands around 1200 cm^{-1} in hexatriene, heptatriene, and octatriene is largely independent of methylation and their intensity considerably weaker. From this together with the position and intensity of the bands at 1146 cm^{-1} in *E*-DMH and 1151 cm^{-1} in *Z*-DMH, it seems reasonable to assign these bands to the same vibrational mode as the above-mentioned 1106-, 1125-, and 1136- cm^{-1} bands in hexatriene, heptatriene, and octatriene. With the low concentration of triplet molecules in the transient experiments, we only expect to see Raman bands that are resonance-enhanced. With Raman excitation at 315 nm we are in resonance with a $T_n \leftarrow T_1$ transition. This electronic transition involves the conjugated π electron system, and consequently vibrations involving in-chain C=C and C-C stretches are expected to be mostly enhanced. We now turn to the question of a more detailed assignment of the particular band around 1150 cm^{-1} . As judged from assignments of ground-state Raman spectra the dominant contributions to Raman bands in the region 1100–1300 cm^{-1} come from C-C single-bond stretching and CCH rocking vibrations, the latter ones usually being found at higher wavenumbers than the former ones. Additionally, a comparison of the structure of hexatriene, heptatriene, octatriene, and dimethylhexatriene points in the direction that the 1100–1150- cm^{-1} vibrational mode is likely to involve either CCH rocking modes at the central H atoms and/or C-C stretching vibrations between the central in-chain carbon atoms.

The latter assignment seems the most likely for two reasons: Firstly, the most recent theoretical calculations agree on the diallylic form being the most stable form in the triplet state of hexatriene, hence implying that the central CC bond is the longest one having most single bond character.^{1,17} Secondly, an analysis of the ground-state Raman spectra obtained from neat samples

with the scanning Raman spectrometer⁵⁵ suggests that for ground-state *E*-DMH bands at 1315 and 846 cm^{-1} can be assigned to coupled C-CH₃ and in-chain C-C single bond stretching vibrations, this coupling leading to the absence of a band in the region 1100–1200 cm^{-1} where the C-C single bond stretching band for polyenes usually is found. With bands of considerable intensity observed at 1151/1146 cm^{-1} in the triplet spectra of *Z*-DMH and *E*-DMH this coupling does not seem to be active in triplet *Z*-DMH and *E*-DMH, which could possibly indicate that the C-C single bond active in the 1151/1146- cm^{-1} normal mode is not adjacent to the methyl groups and hence must be at the center of the molecule. As these experimental observations correspond well with the theoretical predictions, we very tentatively assign the band around 1150 cm^{-1} to a stretching mode of the central CC bond, being aware that further measurements are needed to support this. The decoupling mentioned may also be involved in the relatively large shift of the C=C double bond stretch going from ground state to excited state 2,5-dimethyl-1,3,5-hexatriene. The three bands found from 1200 to 1270 cm^{-1} in the transient spectra of hexatriene, heptatriene, and octatriene, are not found in the triplet spectra of *E*-DMH and *Z*-DMH. The transient bands at 1389 and 1357 cm^{-1} for *E*-DMH, and at 1350 cm^{-1} for *Z*-DMH, are found in a region of methyl deformations and methylene HCH scissoring vibrations. A definite assignment, however, is not possible at present.

Kinetics. Straight lines fit reasonably well with the sets of points in Figure 4 up to delays of 300 ns. The deviations found for delays above 300 ns may be due to errors in the evaluation of the intensity of the transient 1551/1548- cm^{-1} bands that are very weak at longer delays. The deviations may, however, also indicate that the assumption of first-order decay is not fulfilled. The decay kinetics of the triene triplet states in the time-resolved resonance Raman experiments might well be influenced by triplet-triplet annihilation due to high local concentrations generated by the pump laser.

The apparent first-order decay rate constants determined in this work for 0.012 M *E*-DMH from Figure 4A and 0.012 M *Z*-DMH from Figure 4A' are 3–4 times larger than the ones determined by absorption spectroscopy in pulse radiolysis of 0.005 M heptatriene²² and 0.012 M neoalloocimene.¹⁹ However, the apparent lifetimes of 0.003 M *Z*-DMH and of 0.005 M heptatriene determined in both cases by time-resolved resonance Raman spectroscopy are similar.²² Hence, the triplet states of *Z*-DMH and heptatriene might have similar intrinsic lifetimes but be subject to self-quenching. The concentration dependence observed in Figure 4 for the decay of triplet *Z*-DMH corresponds to an apparent rate constant for self-quenching of $\sim 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The apparent rate constants for decay of the triplet states of *E*-DMH and *Z*-DMH at 0.012 M concentration as determined from Figure 4 are somewhat different. However, with the limitations mentioned above this difference seems to us to be within experimental error. Precise measurements, using time-resolved absorption spectroscopy, of the kinetics of triplet *E*-DMH and *Z*-DMH created by both pulse radiolysis and sensitized flash photolysis and including investigations of the concentration dependence of the kinetics would be highly interesting. So would also a knowledge of the exact $T_n \leftarrow T_1$ absorption spectra and extinction coefficients and a thorough steady-state investigation of the triplet-state photochemistry of the two isomers.

Implications for the NEER Principle. The ground states of the *E* and *Z* isomers of 2,5-dimethyl-1,3,5-hexatriene were mentioned above to have different structures around the central C=C double bond and also different conformations around C-C single bonds with *E*-DMH having a planar *s*-trans tEt and *Z*-DMH a nonplanar *s*-cis cZc conformation as the dominant ones. Large differences in UV absorption and Raman spectra resulted from these structural differences.

The triplet-state Raman spectra of *E*-DMH and *Z*-DMH were seen to be very different from the corresponding ground-state Raman spectra. This difference is to be expected with the changes in the electronic structure suggested by the theoretical calculations when going from the ground to the lowest excited triplet state. On the other hand, the triplet-state Raman spectra from the two

Figure 5. Qualitative potential energy surfaces as functions of torsion around the central double bond and of simultaneous torsion around the adjacent single bonds for the ground and lowest excited triplet states of 2,5-dimethyl-1,3,5-hexatriene. The energy surfaces were constructed by combination of empirical functions of the respective torsional angles, $\sin^2 x$ functions being used for bonded interactions and $\exp(-2x^2)$ functions for nonbonded interactions. (Right) Lower surface, ground state; upper surface, triplet state. (Left) Contour map for the surfaces shown on the right hand. Thin lines, ground state; thick lines, triplet state.

isomers were seen to be similar, however, with small differences in wavenumbers, the possible lack of a band close to 1390 cm^{-1} for triplet Z-DMH, and possible differences in intrinsic Raman scattering efficiencies.

The potential energy surfaces for the S_0 and T_1 states of 2,5-dimethyl-1,3,5-hexatriene are ideally functions of all the internal coordinates of the molecule. However, two parameters, viz., the rotation around the central $\text{C}=\text{C}$ double bond and rotation around the adjacent $\text{C}-\text{C}$ single bonds are most important for a description of the differences between the ground-state equilibrium geometries of E-DMH and Z-DMH. The potential energy surfaces along these two parameters are influenced by both bonded and non-bonded interactions, the latter ones being of importance because of the steric hindrance induced by the methyl groups. In the following we hence limit the discussion to potential energy surfaces as functions of the two rotations mentioned, taking into account the influence from steric hindrance. Possible potential energy surfaces for the ground and lowest excited triplet states of 2,5-dimethyl-1,3,5-hexatriene which are qualitatively compatible with the lines of discussion given below are depicted in Figure 5. Purely empirical expressions were used to simulate rotations around the central $\text{C}=\text{C}$ double bond and $\text{C}-\text{C}$ single bonds and the effect of steric hindrance.

The potential energy barrier for rotation around a $\text{C}=\text{C}$ double bond in ground-state 1,3,5-hexatriene is close to 200 kJ/mol .⁷² The barrier for rotation around a $\text{C}-\text{C}$ single bond in ground-state butadiene is $\sim 16\text{ kJ/mol}$.⁷³ With the barrier for twisting around the central $\text{C}=\text{C}$ double bond in the ground state being much larger than the barrier for rotation around the chain $\text{C}-\text{C}$ single bonds, the maximum on the S_0 potential energy surface is likely to be at the same angle of torsion around the central $\text{C}=\text{C}$ double bond for the tEt to tZt transformation as for the cZc to cEc transformation of 2,5-dimethyl-1,3,5-hexatriene (see Figure 5).

The results of the GC analysis indicated similar overall quantum yields for sensitized photoisomerization of E-DMH and Z-DMH. This result is supported by the fact that the negative bands around 1625 , 1300 , and 1035 cm^{-1} in Figure 2D and the positive bands at similar wavenumbers in Figure 2D' are of similar intensity. Under the present conditions the efficiency of energy transfer from the acetone triplet to the trienes is close to unity. Hence, these overall quantum yields reflect the relative intrinsic triplet isomerization yields. Thus the steric hindrance due to the methyl groups apparently does not influence the E-Z isomerization efficiency. This is in agreement with what is observed for stilbene² and the results mentioned above for sensitized photoisomerization of 2,6-dimethyl-2,4,6-octatriene in the absence of a quencher that showed similar yields for conversion to central-E and central-Z

isomers.⁴ The most likely explanation to the similar relative intrinsic triplet isomerization yields is that there is a minimum on the T_1 potential energy surface situated at approximately the same angle of torsion around the central CC bond as the maximum on the S_0 potential energy surface. From the above this angle should then again be common for the two isomers. Other possible minima on the T_1 potential energy surface could correspond to planar geometries with E or Z configuration around the central CC bond.^{2,4} Of these the planar Z geometry is unlikely to correspond to a minimum for reasons of steric hindrance, leaving planar E or twisted geometries as possibilities.

The large differences in ground state properties between E-DMH and Z-DMH, the large differences between the Raman spectra of ground and excited triplet states for each isomer, the similarity of the Raman spectra of their triplet states, and the evidence from GC in combination render the planar E triplet geometry suggested above less likely, and suggest that the triplet geometry with twisting around the central CC bond is the most probable one, in correspondence with the results of theoretical calculations indicating a twisted diallylic structure.^{1,17} However, we cannot exclude that a minor amount of the planar-E triplet is in equilibrium with the twisted triplet, compatible with the model suggested by Butt et al.⁴

Though similar, the triplet Raman spectra from the two isomers nevertheless showed clear differences. With similar angles of rotation around the central CC bond as suggested above, the simplest explanation of the differences in the triplet Raman spectra of E-DMH and Z-DMH is that the differences in conformation around $\text{C}-\text{C}$ single bonds in the ground state are preserved upon excitation to the lowest triplet state. Similar conclusions have previously been formulated for singlet excited states and have been expressed in the NEER principle.^{23,25,26} Our results amount to an extension of the NEER principle from singlet to triplet excited states with much longer lifetimes. Nonequilibration of excited rotamers in the triplet states of 2,5-dimethyl-1,3,5-hexatriene is reasonable, since upon excitation the torsion around the central CC bond and the changes in the electronic system suggested lead to a diallylic structure, where the bonds that are formal single bonds in the ground state acquire more double-bond character. A consequence of the extension of the NEER principle to the triplet state is that E-DMH mainly produces a tPt conformer in the excited triplet state, where P indicates a perpendicular configuration around the central CC bond, whereas Z-DMH mainly produces a cPc conformer (see Figure 5).

In contrast to 2,5-dimethyl-1,3,5-hexatriene the E and Z isomers of 1,3,5-hexatriene are both known to be predominantly s-trans around the $\text{C}-\text{C}$ single bonds.^{23,24,60} The explanation of the differences in the triplet Raman spectra of E-DMH and Z-DMH by the validity of the NEER principle in the excited triplet state implies a prediction of identical triplet Raman spectra from the E and Z isomers of hexatriene. In a series of experiments we have obtained the time-resolved resonance Raman spectra of the triplets produced from the E and Z isomers of 1,3,5-hexatriene.⁷¹ With the same experimental conditions and treatment of data as in the present study we have found that the transient spectra from these two isomers are identical. Hence, the results obtained for 1,3,5-hexatriene and 2,5-dimethyl-1,3,5-hexatriene are in agreement with predictions derived by applying the NEER principle to their lowest excited triplet states.

As mentioned above, the spectra underlying Figure 3 did not show any changes in positions and relative intensities for the two strongest transient Raman bands for delays varying from 50 to 130 ns. A conformational stability for at least 130 ns suggests a lower limit of the rotational barrier around the C_2-C_3 bonds of $\sim 35\text{ kJ/mol}$. This size of the barrier is in between the values cited above for formal $\text{C}-\text{C}$ single and $\text{C}=\text{C}$ double bonds in the ground state and supports the idea of a diallylic structure.

Conclusions

The ground-state UV absorption and Raman spectra presented in this paper confirm that the structures of the E and Z isomers of 2,5-dimethyl-1,3,5-hexatriene are very different. The transient

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Raman spectra and the GC analyses are in agreement with the photochemical reactions expected in the presence of a triplet sensitizer and support the idea that triplet species are intermediates in the sensitized photoisomerizations.

The time-resolved resonance Raman spectra of the lowest triplet states produced from the E and Z isomers of 2,5-dimethyl-1,3,5-hexatriene are similar but show clear differences. On this basis it is concluded that these triplet states must have different geometries or that different mixtures of triplet species are produced from the two isomers. The simplest explanation to this fact is that the triplet species formed from both isomers are twisted around the central carbon-carbon bond and that the differences in conformation around C-C single bonds in the ground state are preserved upon excitation to the lowest triplet state. The twisted geometry corresponds to a diallylic structure and is in agreement with theoretical predictions. Moreover, the preservation of ground-state conformations around C-C single bonds in the excited state indicates that the NEER principle applies to the lowest triplet states of E-DMH and Z-DMH. In addition, through a comparison between hexatriene, heptatriene, octatriene, and 2,5-dimethyl-hexatriene a partial assignment is suggested for the resonance

Raman spectra of the lowest triplet states of these compounds.

Note Added in Proof. Recent investigations⁷⁴ show that cZt rather than cZc is the predominant conformation of (Z)-2,5-dimethyl-1,3,5-hexatriene in the ground state. Although this is different from our assumption in the present paper, our qualitative arguments and conclusions are unaltered by this change.

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Time-Resolved Resonance Raman Spectroscopy of the Lowest Excited Triplet States of the E and Z Isomers of 1,3,5-Hexatriene

Frans W. Langkilde, Niels-Henrik Jensen, and Robert Wilbrandt*

Chemistry Department, Risø National Laboratory, DK-4000 Roskilde, Denmark (Received: June 24, 1986)

The lowest excited triplet states of the E and Z isomers of 1,3,5-hexatriene were produced by laser flash photolysis using acetone as sensitizer. Acetone was excited at a wavelength of 308 nm and the time-resolved resonance Raman spectra of the lowest excited triplet states of the triene isomers were obtained by subsequent probing in resonance with the $T_n \leftarrow T_1$ absorption at 315 nm. The resonance Raman spectra of the triplet states of the two isomers were identical within limits of error. Five transient Raman bands were observed from both isomers. Bands were detected for the E isomer at 1570, 1270, 1234, 1200, and 1106 cm^{-1} and for the Z isomer at 1569, 1270, 1236, 1199, and 1107 cm^{-1} . The apparent first-order decay rate constants of the triplet states were $1.09 \times 10^7 \text{ s}^{-1}$ for (E)-hexatriene and $1.04 \times 10^7 \text{ s}^{-1}$ for (Z)-hexatriene. Ground-state Raman spectra and GC analysis of samples before and after the sensitized photolysis indicated a higher efficiency of $Z \rightarrow E$ than of $E \rightarrow Z$ isomerization from the triplet states. From these overall results a common relaxed geometry of the lowest triplet states of the E and Z isomers of 1,3,5-hexatriene with a twisted central bond seems the most likely structure in solution. Isomerization efficiencies suggest that the structure of the twisted triplet species is closer to that of the E than to that of the Z isomer.

1. Introduction

Short polyenes have attracted renewed interest in the past decade.¹ The state ordering of the singlet manifold has been the main issue in these studies. Another fundamental question, albeit less extensively studied, is that of the properties of the potential energy surfaces in ground and excited states.

1,3,5-Hexatriene is the simplest polyene with a central double bond and therefore of particular fundamental interest. Of the two isomers, (E)-1,3,5-hexatriene (E-HT) is known to have a predominantly planar tEt conformation with respect to double and single bonds in the ground state, whereas (Z)-1,3,5-hexatriene (Z-HT) has been reported to have a tZt conformation being twisted by 10° around the central double bond.² Additional less stable s-cis conformers have been found in low-temperature matrix isolation studies.^{3,4}

Of the excited singlet states of hexatriene the $1^1B_u^+$ state is the one best characterized by optical absorption,⁵⁻⁷ electron loss,⁸ and preresonance Raman⁹ spectroscopy, whereas attempts to locate the $2^1A_g^-$ state have been unsuccessful¹⁰ partly because of the complete absence of fluorescence from hexatriene.⁶ The question of state ordering is still a matter of discussion, and the potential energy surfaces in both the $1^1B_u^+$ and the $2^1A_g^-$ states are largely unknown from an experimental point of view.

The triplet states of hexatriene have been studied by direct singlet-triplet absorption^{5,11} and electron loss spectroscopy.⁸ From the former the vertical triplet energy of the lowest triplet state

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