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Resonance Raman and Absorption Spectroscopy of 2- and 3-Methyl-1,3,5-hexatriene in the T₁ State. Steric Control of Excited-State Molecular Structure

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Resonance Raman (RR) spectra of (E)-2-methyl-1,3,5-hexatriene ([E]-2-MHT), (E)-4-deutério-2-methyl-1,3,5-hexatriene ([E]-2-MHT-4-d), (Z)-2-methyl-1,3,5-hexatriene ([Z]-2-MHT), (E)-3-methyl-1,3,5-hexatriene ([E]-3-MHT), and (Z)-3-methyl-1,3,5-hexatriene ([Z]-3-MHT) in the lowest triplet state T₁ are reported and discussed. QCFF/PI calculations are performed to determine energies and optimized geometries in the S₀, T₀, and T₁ electronic states. For each T₁ species, T₁ → T₂ transitions, vibrational frequencies, and RR intensities are calculated and compared with the observed frequencies and intensities. The ground-state distribution of rotamers is shown to be preserved upon excitation to T₁ and during the T₁ lifetime (NEER principle). In contrast, the E and Z isomers associated with the torsion around the central C=C bond are found to equilibrate in T₁ according to the Boltzmann rule. In 2-MHT, the T₁ RR spectrum is attributed to both the E and Z forms, the former being dominant. For (E)-2-MHT, only the E conformer is shown to be present, whereas for (Z)-2-MHT the contribution of the Z conformer is demonstrated. The T₁ RR spectrum of 3-MHT receives a larger contribution from the Z than from the E isomer. The spectra obtained from (E)-3-MHT and (Z)-3-MHT are identical, since in both isomers the E conformer is present. Measurements of time-resolved triplet–triplet absorption as a function of temperature yield activation energies and frequency factors for the decay of the T₁ state of (E)-2-MHT and (Z)-3-MHT. The implications of these results on the shape of the T₁ potential energy curves are discussed.

I. Introduction

Polyenes are important both in chemistry and biology. One of their main reactions is the isomerization around the C=C double bond. In isomerization studies of polyenes, 1,3,5-hexatriene is a model compound, since it is the smallest polyene with both terminal and internal C=C double bonds, and its photophysics and photochemistry have been subjected to extensive study.

For alkyl-substituted 1,3,5-hexatrienes, steric interaction influences the molecular structure in the electronic ground state S₀ with respect to the in-plane CCC bond angles, the torsion around the C-C single bonds, and the degree of planarity of the molecule. Planar molecules, one can distinguish between s-trans (t) and s-cis(c) rotamers at the CC single bonds. In addition, the molecules may be more or less twisted around the CC single bonds and the central C=C double bond. For the latter bond, we shall here denote the 90° twisted configuration by P for perpendicular. The geometries that are perpendicular at the central CC bond are relevant only for electronic excited states, not for the ground state.

The abundance of different rotamers of 1,3,5-hexatrienes in S₀ is determined by the electronic structure and by steric interactions. Differences in CC single-bond conformation are reflected in differences in UV absorption spectra and in the singlet-state photochemistry taking place after direct excitation. The dominant products in the singlet photochemistry of 1,3,5-hexatrienes are 1,3-cyclohexadiene, 1-allylcyclopropene, bicyclo[3.1.0]hex-2-ene, and 2-vinyl-1-methylene cyclopropane, whereas the quantum yield of E ↔ Z isomerization is low, except in highly substituted compounds. The singlet photochemistry has in part been rationalized by invoking the principle of nonequilibrium of excited rotamers (NEER), which states that the geometry around formal CC single bonds is preserved after excitation to the excited singlet state. In contrast, the sensitized photochemistry of 1,3,5-hexatriene in the triplet state leads primarily to isomerization. The triplet photoisomerization proceeds through the lowest excited triplet state T₁, which has been found to have a lifetime of 100–300 ns. In a series of papers, we have studied the T₁ state of 1,3,5-hexatriene and methyl-substituted derivatives using time-resolved absorption and resonance Raman (RR) spectroscopy, in order to map the T₁ potential energy surface (PES) with respect to torsion around the central C=C double bond and the CC single bonds. The above-mentioned NEER principle was found to apply to the T₁ state as well, i.e., even with the relatively long triplet lifetimes the geometry around the CC single bonds is preserved.

In order to explore the potential energy curve for the torsional coordinate around the central C=C bond, we have compared the RR and absorption spectra, and the singlet-state photophysics, of 2- and 3-MHT.

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(15) Manuscript in preparation.
forms in the TI state populate isoenergetic minima in Figure 1. The ground-state (E)-2-MHT, (E)-2-MHT-4-d, (Z)-2-MHT, (E)-3-MHT, and (Z)-3-MHT have not been published before.

In the present paper we report the time-resolved RR spectra of the lowest excited triplet state T1 from (E)-2-MHT, (E)-2-MHT-4-d, (Z)-2-MHT, (E)-3-MHT, and (Z)-3-MHT using a pump–probe technique with two pulsed lasers. The triplet state is populated by excitation of acetone as sensitizer and probed in resonance with a T1 → T1 transition of 2- and 3-MHT around 315 nm. The frequencies of the T1 RR bands are calculated with the modified version of the QCFF/PI program. The T1 RR intensities are determined on the basis of the change in equilibrium geometry between the T1 state and the T1 state of the dominant T1 → T1 transition. The activation energy of the decay of T1 is determined by time-resolved UV absorption measurements for (E)-2-MHT and (Z)-3-MHT as a function of temperature (293–187 K).

II. Experimental Methods

A. Materials. Acenonitrile (Merck, LiChrosolv), acenonitrile-d3 (Fluka, puriss., >99.8% D or Fluka, purum, >99% D), methanol (Merck, p.a.), and acetone (Merck, p.a.) were used as received. The synthesis of (E)-2-MHT, (E)-2-MHT-4-d, (Z)-2-MHT, (E)-3-MHT, and (Z)-3-MHT has been described in detail previously.1,8 The purity of the samples was analyzed by gas chromatography (GC, He carrier gas, capillary column, BP10 at 62 °C or DB1 at 38 °C). The samples of (E)-2-MHT and (E)-2-MHT-4-d showed no detectable impurities. The sample of (Z)-2-MHT was 98% pure (4% (E)-2-MHT), the (E)-3-MHT sample was 98% pure (2% (Z)-3-MHT), and the (Z)-3-MHT sample was 98% pure (4% (E)-3-MHT and 2-methyl-1,3-cyclohexadiene).

After preparative GC, the samples were captured in capillary glass tubes in a cold trap under reduced pressure (ca. 0.1 mm Hg); the capillaries were sealed and kept in a freezer. 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 more than 35 min.

B. Raman Measurements. The ground-state Raman spectra of (E)-2-MHT, (E)-2-MHT-4-d, (E)-3-MHT, and (Z)-3-MHT were recorded according to procedures described in ref 18. For (Z)-2-MHT, the Raman spectrum was recorded as described in ref 19 and the Fourier transform infrared spectrum of a matrix isolated sample (Ar, 15 K; not shown) as described in ref 18. The time-resolved T1 RR spectra were obtained at room temperature as described previously.1,10,12 The triplet state of the triene was produced by exciting acetone as sensitizer with a pump pulse from an excimer laser (Lambda Physics EMG 1025) at 308 nm (ca. 5 mJ per pulse at the sample). The RR spectrum of the triene T1 state was obtained with the second harmonic at 315.8 nm (317.5 nm for (E)-2-MHT-4-d) from a Nd:YAG pumped dye laser (Quantel) as probe pulse (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 triplet-state RR spectra were obtained by subtraction procedures.

The sample was contained in a spinning cylindrical Suprasil cell with 26-mm inner diameter and 6-mm inner height. The detection system has been described in detail previously.9,10,12 Scattered Raman light was dispersed in a single grating spectrometer (f = 600 mm, 2400 grooves/mm). A polarization scrambler was placed in front of the spectrometer. For (E)-2-MHT, (Z)-2-MHT, (E)-3-MHT, and (Z)-3-MHT, a homebuilt intensified vidicon detector with 300 channels was used, whereas for (E)-2-MHT-4-d an intensified photodiode array (OSMA IR4-700 from Spectroscopy Instruments) with 700 active channels was used.12

Figure 1. Ground-state molecular structure of (E)-2-methyl-1,3,5-hexatriene ((E)-2-MHT), (E)-4-deutério-2-methyl-1,3,5-hexatriene ((E)-2-MHT-4-d), (Z)-2-methyl-1,3,5-hexatriene ((Z)-2-MHT), (E)-3-methyl-1,3,5-hexatriene ((E)-3-MHT), and (Z)-3-methyl-1,3,5-hexatriene ((Z)-3-MHT).

Wavenumber/cm\(^{-1}\)

Figure 2. Ground-state Raman spectra (514.5 nm excitation) of neat (A) (E)-2-MHT, (B) (Z)-2-MHT, (C) (E)-2-MHT-4-d, (D) (E)-3-MHT, and (E) (Z)-3-MHT.

The chemical composition of the solutions was monitored by GC before the laser experiments to ensure purity and after the experiments to follow isomeric conversion during the laser flash photolysis. The conversion between the 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. The procedures used in the time-resolved UV absorption measurements have been described in detail previously.\(^{12}\) The sample was irradiated with a pulse from the excimer laser at 308 nm, with a pulse energy of ca. 20 mJ at the sample. The triplet-triplet absorption at 320 nm was measured at right angles to the laser beam with a pulsed Xe lamp, a monochromator (spectral bandpass 8 nm) placed after the cell, and a photomultiplier (RCA 1P28) coupled to a digital storage oscilloscope (DSC). The LeCroy 9400 DSC used previously\(^{12}\) was replaced with a LeCroy 9450 DSC with a higher time-resolution. The absorbance at 308 nm from the acetone sensitizer was ca. 1 per cm. The sample cell and cooling procedures were as described previously.\(^{15}\) Like for the Raman measurements, the chemical composition of the solutions was monitored by GC before and after the experiments.

III. Experimental Results

A. Ground State. The ground-state Raman spectra of neat (E)-2-MHT, (Z)-2-MHT, (E)-2-MHT-4-d, (E)-3-MHT, and (Z)-3-MHT, with 514.5-nm CW excitation, are shown in Figure 2A-E, respectively. The frequencies of the E isomers have been published previously;\(^\text{18}\) those of (Z)-2-MHT and (Z)-3-MHT are reported in Table I, for (Z)-2-MHT together with infrared frequencies of a matrix-isolated sample. In addition to the bands listed in Table I, the matrix-isolated sample showed several infrared bands of medium intensity around 1600, 1450, and 1000 cm\(^{-1}\). The additional bands may be related to the presence of two rotameric species, or to the population of different sites in the Ar matrix. Also included in Table I is an empirical assignment of the vibrational spectra of (Z)-2-MHT and (Z)-3-MHT, obtained from comparison with spectra of (Z)-1,3,5-hexatriene (ZHT),\(^{19,20}\) (E)-2-MHT, and (E)-3-MHT.\(^{18}\)

B. Triplet State. Raman experiments are reported for the following Ar-saturated solutions, containing 0.545 M acetone as sensitizer: (1) 0.010 M (E)-2-MHT in CH\(_3\)CN, (2) 0.007 M (E)-2-MHT in CD\(_3\)CN, (3) 0.008 M (E)-2-MHT-4-d in CH\(_3\)CN, (4) 0.008 M (E)-2-MHT in CD\(_3\)CN, (5) 0.010 M (Z)-2-MHT in CD\(_3\)CN, (6) 0.004 M (E)-3-MHT in CH\(_3\)CN, (7) 0.006 M (E)-3-MHT in CD\(_3\)CN, (8) 0.007 M (Z)-3-MHT in CH\(_3\)CN, and (9) 0.003 M (Z)-3-MHT in CD\(_3\)CN. In the time-resolved absorption measurements the solutions were (10) 0.408 M acetone and 0.008 M (E)-2-MHT in methanol and (11) 0.408 M acetone and 0.0015 M (Z)-3-MHT in methanol.

Subtraction techniques used in the RR spectra have been discussed in detail previously.\(^{9,10}\) Each sample cell was used to obtain spectra using (a) the probe laser only; (b) both pump and

TABLE II: Observed Frequency (cm⁻¹) and Intensity of Raman Bands of the Lowest Excited Triplet State of (E)-2-MHT, (E)-2-MHT-4-d, (Z)-2-MHT, (E)-3-MHT, and (Z)-3-MHT

<table>
<thead>
<tr>
<th>Compound</th>
<th>E-2-MHT 315.8 nm CH₃CN/CD₃CN</th>
<th>(E)-2-MHT-4-d 317.5 nm CH₃CN/CD₃CN</th>
<th>(Z)-2-MHT 315.8 nm CD₂CN</th>
<th>(E)-2-MHT 315.8 nm CD₂CN</th>
<th>(Z)-2-MHT 315.8 nm CD₂CN</th>
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<tr>
<td>Frequency</td>
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<td>1559 s</td>
<td>1557 s</td>
<td>1558 s</td>
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<tr>
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<td>1427 w</td>
<td>1441 w</td>
<td>1437 w</td>
<td>1434 w</td>
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<td></td>
<td>940 w</td>
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<tr>
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<td>1094 m</td>
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<tr>
<td></td>
<td>942 w</td>
<td>902 m</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>823 m</td>
<td>1103 m</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Solvent and excitation wavelength listed.

TABLE III: Energies (kcal/mol) of Optimized Geometries of the Various Isomeric Forms of 2-MHT Relative to the eEt Form in the States Sₗ, Tₐ, and Tₜ (n = 5, 6, 7; See Text)

<table>
<thead>
<tr>
<th>State</th>
<th>Sₗ</th>
<th>Tₐ</th>
<th>Tₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>eEt</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>cEt</td>
<td>-0.4</td>
<td>0.4</td>
<td>-0.5</td>
</tr>
<tr>
<td>tZt</td>
<td>-4.5</td>
<td>3.8</td>
<td>-2.2</td>
</tr>
<tr>
<td>cZt</td>
<td>-4.4</td>
<td>4.2</td>
<td>-1.2</td>
</tr>
<tr>
<td>tPt</td>
<td>-6.5</td>
<td>6.5</td>
<td>34.9</td>
</tr>
<tr>
<td>cPt</td>
<td>6.8</td>
<td>-6.8</td>
<td>35.6</td>
</tr>
</tbody>
</table>

TABLE IV: Energies (kcal/mol) of Optimized Geometries of the Various Isomeric Forms of 3-MHT Relative to the eEt Form in the States Sₗ, Tₐ, and Tₜ (n = 5, 6, 6; See Text)

<table>
<thead>
<tr>
<th>State</th>
<th>Sₗ</th>
<th>Tₐ</th>
<th>Tₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>eEt</td>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>tZt</td>
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<td>-0.5</td>
<td>-3.1</td>
</tr>
<tr>
<td>tPt</td>
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<td>4.6</td>
<td>32.8</td>
</tr>
</tbody>
</table>

TABLE V: Calculated Energies (eV) for Tₐ → Tₜ Transition with Largest Oscillator Strength of the Various Isomeric Forms of 2-MHT and 3-MHT

<table>
<thead>
<tr>
<th>Compound</th>
<th>2-MHT</th>
<th>3-MHT</th>
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<tbody>
<tr>
<td>eEt</td>
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<td>5</td>
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<tr>
<td>cEt</td>
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<td>4.13</td>
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<tr>
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<td>5</td>
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<tr>
<td>cZt</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>tPt</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>cPt</td>
<td>7</td>
<td>7</td>
</tr>
</tbody>
</table>

± 0.2 kcal/mol and A = (2.7 ± 0.6) × 10⁻² s⁻¹. The first-order decay at 213 K of the triplet–triplet absorption is illustrated for (E)-2-MHT by the inset in Figure 5. An increase in the buildup time of the triplet was observed with decreasing temperature.

IV. Theoretical Results

Calculations were performed using a modified version of the semiempirical quantum mechanical consistent force field QCFF/PI program, as described previously. Theoretical results from the QCFF/PI calculations are reported in Tables III–VI and in the supplementary material. In Table III is listed energies of the various optimized isomeric forms of 2-MHT relative to the eEt form in the Sₗ, Tₐ, and Tₜ states. The corresponding energies of 3-MHT are reported in Table IV. For each geometry, the Tₜ
state with the largest $T_1 \rightarrow T_0$ transition oscillator strength is indicated in Table V, together with the energy of the $T_1 \rightarrow T_2$ transition. Calculated geometries for the various isomers and rotamers of 2-MHT and 3-MHT in the $S_0$, $T_1$, and $T_2$ states are reported in the supplementary material.

Vibrational frequencies were calculated for all the relevant $T_1$ geometries of (E)-2-MHT, (E)-2-MHT-4-d, (Z)-2-MHT, (E)-3-MHT, and (Z)-3-MHT, i.e., the local minima on the $T_1$ PES. These frequencies are listed in Table VI or in the supplementary material.

Under the assumption of a predominant Franck-Condon mechanism of RR scattering, the RR intensities can be expressed by the $\gamma$ factors, calculated from the change in equilibrium geometry between $T_1$ and $T_0$. The calculated $\gamma$ factors are listed together with the vibrational frequencies in Table VI and in the supplementary material. The data in Table VI can be used to construct theoretical RR spectra of the $T_1$ state for the various compounds and geometries. This is done in Figure 6 for (E)-2-MHT, in Figure 7 for (E)-2-MHT-4-d, in Figure 8 for (Z)-2-MHT, and in Figure 9 for (E)-3-MHT and (Z)-3-MHT. The calculated RR spectra are shown together with the experimentally observed spectra to allow a direct comparison.

V. Discussion

In the ground-state $S_0$ of 1,3,5-hexatriene, the $s$-trans conformation ($tEt$ and $iEt$) at the C-C single bonds is favored over the $s$-cis form, since in the latter conformation nonbonded electron pairs which repel each other are brought close together. This preference for $s$-trans conformation is opposed by methyl substitution, in particular for $Z$ isomers, due to the steric repulsion of the methyl hydrogens. For (Z)-2,5-dimethyl-1,3,5-hexatriene (cZt), an $s$-cis conformation at one of the C-C single bonds is induced. For substitution of only one methyl group, as in 2-MHT and 3-MHT, the modifications of the molecular structure are less pronounced.

At room temperature, a $tEt$ structure has been found experimentally for (E)-2-MHT (see Figure 1), whereas for (Z)-2-MHT a $2:1$ equilibrium between the $tZt$ and $cZt$ forms has been found. The planar $Z$ geometry is found at room temperature in the $tEt$ and $iEt$ forms. It should be noted that for the $E$ isomer the lateral methyl group causes more steric hindrance in the 3- than in the 2-position, whereas for the $Z$ isomer it causes more steric hindrance in the 2- than in the 3-position. As a consequence, the $cZt$ form of 2-MHT deviates strongly from planarity.

A. Calculated Energies and Geometries of Ground and Excited States. Energy minima, calculated for 2-MHT and 3-MHT in the $S_0$, $T_1$, and $T_2$ states, are reported in Tables III and IV. The ground-state energy of 2-MHT in Table III is calculated to be slightly lower for the $cEt$ than for the $tEt$ (by 0.8 kcal/mol), and for the $cZt$ than for the $iZt$ (by 0.1 kcal/mol) forms. This disagreement with the experimental results can be ascribed to the tendency of the QCFF/PI calculation to overestimate the steric hindrance connected with methyl groups compared to terminal methylene groups. A corresponding discrepancy has been found previously in the study of 2,5-dimethyl-1,3,5-hexatriene. The ordering is reversed in the $T_1$ state. In the $T_2$ state of 2-MHT, the ordering is similar to that of $S_0$, but with a much bigger difference between the $iZt$ and $cZt$ forms. In the $T_1$ state, the planar $Z$ geometry is calculated to be somewhat higher than the planar $E$ geometry, and the $P$ geometry even higher.

Whereas for 2-MHT (Table III) the planar $Z$ geometry is clearly higher in energy than the planar $E$ geometry in the $S_0$ and
Steric Control of Excited-State Molecular Structure


Figure 5. Arrhenius plot (O) of the decay rate constant of the 2-methyl-1,3,5-hexatriene T\textsubscript{1} state for Ar-saturated methanol solution of 0.408 M acetone and 0.008 M (E)-2-MHT and Arrhenius plot (●) of the decay rate constant of the 3-methyl-1,3,5-hexatriene T\textsubscript{1} state for Ar-saturated methanol solution of 0.408 M acetone and 0.015 M (Z)-3-MHT. Inset: Time-resolved triplet-triplet absorption of (E)-2-MHT at 213 K, monitored at 320 nm. Pump wavelength 308 nm.

1/T * 1000 (K\textsuperscript{-1})


<table>
<thead>
<tr>
<th>1/T * 1000 (K\textsuperscript{-1})</th>
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<tbody>
<tr>
<td>6.0</td>
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<td>6.2</td>
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</tr>
<tr>
<td>7.0</td>
</tr>
</tbody>
</table>

T\textsubscript{1} states, the planar E and Z geometries of 3-MHT are very close in energy in the S\textsubscript{0} and T\textsubscript{1} states (Table IV). In both T\textsubscript{1} and T\textsubscript{2}, the P geometry of 3-MHT is clearly above the planar geometries.

From Table V it appears that for the planar E and Z forms of both 2-MHT and 3-MHT, the strongest T\textsubscript{1} \rightarrow T\textsubscript{1} transition is for n = 5, and the transition energy is in the region 3.93-4.19 eV, corresponding to 315-296 nm. For the P forms, the transition energy is 5.4 eV, corresponding to 230 nm, which is clearly out of resonance with the experimental RR excitation around 315 nm.

The calculated optimized molecular geometries are reported in the supplementary material; we shall now discuss briefly the most important features. In the ground-state S\textsubscript{0}, both optimized geometries of 3-MHT are planar, whereas for 2-MHT the c\textsubscript{Zt} form is nonplanar. The optimized geometries of 2-MHT are characterized by large C\textsubscript{2}C\textsubscript{3}C\textsubscript{4} angles for the t\textsubscript{Et} and c\textsubscript{Et} forms and very large C\textsubscript{2}C\textsubscript{3}C\textsubscript{4} and C\textsubscript{3}C\textsubscript{4}C\textsubscript{5} angles for the t\textsubscript{Zt} and c\textsubscript{Zt} forms. For both forms of 3-MHT, the C\textsubscript{1}C\textsubscript{2}C\textsubscript{3} and C\textsubscript{3}C\textsubscript{4}C\textsubscript{5} angles are rather large.

In the T\textsubscript{1} state, the c\textsubscript{Zt} geometry of 2-MHT is twisted by 30° around the central CC bond, whereas for 2-MHT the c\textsubscript{Zt} form is nonplanar. The optimized geometries of 2-MHT are characterized by large C\textsubscript{2}C\textsubscript{3}C\textsubscript{4} angles for the t\textsubscript{Et} and c\textsubscript{Et} forms and very large C\textsubscript{2}C\textsubscript{3}C\textsubscript{4} and C\textsubscript{3}C\textsubscript{4}C\textsubscript{5} angles for the t\textsubscript{Zt} and c\textsubscript{Zt} forms. For both forms of 3-MHT, the C\textsubscript{1}C\textsubscript{2}C\textsubscript{3} and C\textsubscript{3}C\textsubscript{4}C\textsubscript{5} angles are rather large.

In the T\textsubscript{1} state, all bond lengths turn out to be similar, slightly above 1.4 Å for all CC bonds of both 2-MHT and 3-MHT, apart from the P isomers where the length of the central CC bond is 1.47 Å, corresponding to a ground-state C\textsubscript{1}C\textsubscript{2}C\textsubscript{3}C\textsubscript{4} bond, for all forms. For both 2-MHT and 3-MHT, the in-plane CCC angles change very little between S\textsubscript{0} and T\textsubscript{1}.

In the T\textsubscript{2} state, all bond lengths turn out to be similar, slightly above 1.4 Å for all CC bonds of both 2-MHT and 3-MHT, apart from the P isomers where the length of the central CC bond is 1.47 Å. For 3-MHT, the CCC (in-plane) and CCCC (out-of-plane) angles are similar to those of the T\textsubscript{1} state. For 2-MHT, the CCC angles are similar to those of the T\textsubscript{1} state. For the c\textsubscript{Zt} form of 2-MHT, the torsion at the C\textsubscript{2}C\textsubscript{3} bond decreases between T\textsubscript{1} and T\textsubscript{2} and is replaced by a torsion at the C\textsubscript{3}C\textsubscript{4}C\textsubscript{5} bond in T\textsubscript{2}.

B. Ground-State Raman Spectra. Ground-state Raman spectra are shown in Figure 2. Figure 2 also shows the changes in...
The normal modes dominated by C-C stretches, and strongly coupled to CH in-plane rocks, have been shown for (E)-2-MHT and (Z)-2-MHT to couple and split into bands above 1300, around 1000-777 cm⁻¹ for (E)-2-MHT, 990-803 cm⁻¹ for (E)-3-MHT, and 942-785 cm⁻¹ for (E)-3-MHT. This splitting seems to be operative of deuteriated derivatives of 2,5-dimethyl-1,3,5-hexatriene.\(^{12}\) Whereas the vibrational pattern of (E)-2-MHT is influenced strongly by the lateral methyl group and is dominated by local symmetry coordinates, that of (E)-3-MHT is influenced less by the lateral methyl group and is dominated by global symmetry coordinates like the ones for unsubstituted (E)-1,3,5-hexatriene. However, the observation of the weak splitting for (Z)-3-MHT is not reproduced by QCFF/PI calculations. Using the unmodified version of the QCFF/PI program,\(^{16,17}\) we found the above-mentioned splitting with the lowest frequency C-C stretching modes at 841 cm⁻¹ for (E)-2-MHT and 820 cm⁻¹ for (Z)-2-MHT.

C. Triplet Raman Spectra. NEER Principle. The discussion of the T₁ RR spectra shall be divided in two sections. In the present section we discuss the role of conformers associated with the C₁C₃ and C₄C₅ bonds, on the basis of experimental results and with relation to the principle of nonequilibrium of excited-state rotamers (NEER). In the following section we shall discuss the contribution of the different E, Z, and P isomers by comparison between calculated and experimental RR spectra.

The NEER principle was originally introduced for the S₁ state of 1,3,5-hexatrienes, and its validity was in part explained on the basis of their short S₁ lifetime.\(^{1}\) Later, identical T₁ RR spectra were observed for the E and Z isomers of 1,3,5-hexatriene,\(^{10}\) whereas for 2,5-dimethyl-1,3,5-hexatriene different T₁ RR spectra were observed for the E and Z isomers.\(^{9}\) This difference was explained by extending the validity of the NEER principle to the T₁ state, a conclusion which was strongly supported in a study of deuteriated derivatives of 2,5-dimethyl-1,3,5-hexatriene.\(^{13}\)

According to the NEER principle, the distribution of different conformers in the ground state is preserved upon excitation to the
Differences at 1322, 1226, and 1154 cm⁻¹ being easily explained on the NEER principle and clearly demonstrates that the NEER ground-state (E)-2-MHT and (Z)-ZMHT. This is indeed obquently, we expect different RR spectra starting from to be populated in TI, the actual distribution being determined in part by the steric hindrance from the methyl group, which is larger for the (Z)-2-MHT, with a 2:1 equilibrium mixture between tZt and cZt species, where X indicates E, Z, or P configuration at the central CC bond. The population distribution between tEt, tZt, and tPt is determined by their relative energy, which again in part is determined by the amount of steric hindrance from the methyl group, which is larger for the tEt than for the tZt triplet geometry. Consequently, we expect identical TI RR spectra from (E)- and (Z)-3-MHT. This is indeed the case, as seen from spectra 4A and 4C (4B and 4D). The two spectra are identical within experimental uncertainty, small differences at 1322, 1226, and 1154 cm⁻¹ being easily explained by differences in the ground-state Raman spectra of (E)-3-MHT and (Z)-3-MHT, together with the experimental triplet-state time-resolved resonance Raman spectrum (spectrum 4C). The γ values for the tPt form cannot be compared directly with those of the cEt and cZt forms.

T₁ state. Consequently, on the basis of the above-mentioned ground-state forms and the NEER principle, it is possible to make predictions concerning the population of excited-state species. Since they have tEt and tZt ground-state geometries, (E)-3-MHT and (Z)-3-MHT are expected to yield in T₁ the same population distribution between cEt and cZt species, where X indicates E, Z, or P configuration at the central CC bond. The population distribution between tEt, tZt, and tPt is determined by their relative energy, which again in part is determined by the amount of steric hindrance from the methyl group, which is larger for the tEt than for the tZt triplet geometry. Consequently, we expect identical T₁ RR spectra from (E)- and (Z)-3-MHT. This is indeed the case, as seen from spectra 4A and 4C (4B and 4D). The two spectra are identical within experimental uncertainty, small differences at 1322, 1226, and 1154 cm⁻¹ being easily explained by differences in the ground-state Raman spectra of (E)-3-MHT and (Z)-3-MHT (Figure 2E).

Starting from (E)-2-MHT (tEt in S₀), tEt species are expected to be populated in T₁, the actual distribution being determined in part by the steric hindrance from the methyl group, which is larger for the tZt than for the tEt triplet geometry. Starting from (Z)-2-MHT, with a 2:1 equilibrium mixture between tZt and cZt in S₀, we expect mainly tZt forms to be populated in T₁, as for (E)-2-MHT but also a substantial part of cZt species. Consequently, we expect different T₁ RR spectra starting from ground-state (E)-2-MHT and (Z)-2-MHT. This is indeed observed in Figure 3, where spectra 3A and 3B are clearly different. Thus, the two isomers of 3-MHT yield identical triplet spectra, whereas the spectra of the two isomers of 2-MHT are different. For both compounds, this is in agreement with predictions based on the NEER principle and clearly demonstrates that the NEER principle applies to 2-MHT and 3-MHT.

Apart from the differences between spectra 3A and 3B, several bands are common to the two spectra. From the mentioned 2:1 equilibrium of (Z)-2-MHT, spectra 3A and 3B are best explained as due to common tEt species, with an additional contribution in spectrum 3B from cEt species. Spectrum 3A was subtracted from spectrum 3B, after proper rescaling to make common bands match in intensity, to check this possibility. The result is shown in Figure 3C. Spectrum 3C is thus believed to be due to the cEt forms of (Z)-2-MHT in the T₁ state. It is shown below that spectrum 3C is indeed very similar to the spectrum calculated for this species. Thus, the results shown in Figures 3 and 4 yield very strong evidence of the validity of the NEER principle for the T₁ state of 2-MHT and 3-MHT.

D. Triplet Raman Spectra. E and Z Species. The results of the previous section indicate that the validity of the NEER principle in the T₁ state of 2-MHT and 3-MHT is so firmly established that in the discussion of other aspects of the T₁ geometry we can confine ourselves to the subset of geometries that are allowed by the NEER principle. The discussion will be based on the comparison between calculated and observed T₁ RR spectra in Figures 6–9. As shall be seen, it is possible to assign the observed vibrational bands to the calculated ones quite unambiguously. A full assignment of all the observed frequencies and intensities of Table II to the calculated frequencies and γ factors of Table VI will not be attempted; only the strongest bands will be assigned.

Another general problem relates to the possible population in T₁ of P geometries. In previous studies of 1,3,5-hexatriene and 2,5-dimethyl-1,3,5-hexatriene, we have not found any positive confirmation that P forms are populated. In all cases we have
been able to explain the observed spectra with the spectra calculated for the planar E and Z forms, without ever having to invoke the spectra calculated for the P form to account for the experimental spectra. In some cases, but definitely not all, we have been able to state that calculated bands of high intensity belonging to the P form are unobserved in experiment. It thus seems unlikely that P forms contribute to the experimental spectra in previous studies. However, this does not necessarily mean that the P forms are not populated, for the following reason. The strongest T1 → T0 transition has been calculated at around 4.2 eV, corresponding to ca. 300 nm, for the planar E and Z forms, whereas for the P form it is calculated at around 5.5 eV, corresponding to ca. 230 nm.11,12 With a probe laser wavelength of around 315 nm, the resonance Raman conditions are fulfilled for the planar E and Z forms, not for the P form. Thus, P forms may be present without contributing significantly to the observed RR spectra. From the planar E form in the time-resolved T1, RR spectra, we determined a population ratio NE/NP ≫ 0.01 for DMHT in the T1 state.13

These arguments apply equally well to the present study of 2-MHT and 3-MHT. As seen from Table V, the T1 → T0 transition energies of the planar E and Z forms are calculated at around 4.1 eV, those of the P forms at around 5.4 eV, and we shall see below that the experimental spectra can be understood on the basis of the spectra calculated for the planar E and Z geometries alone.

(E)-2-MHT. The observed T1, RR spectrum of (E)-2-MHT is shown in Figure 6 together with the spectra calculated for the tEt, tPe, and ZtZ forms of 2-MHT. From previous studies of E- and Z-1,3,5-hexatriene we know that equilibration around the central CC bond is fast, and the equilibrium between the planar (e.g., the planar E and Z forms) is established within the triplet lifetime. Thus, the distribution between planar E and Z forms is determined by their relative energies through the Boltzmann equation.

For 1,3,5-hexatriene in the T1 state, we calculated the planar Z form to be 1.1 kcal/mol above planar E, corresponding to Z:E ratios of 0.15 at 293 K and 0.05 at 183 K. Experimentally, however, we found the two forms to be nearly isoenergetic, with a Z:E ratio close to unity. For 2-MHT, we calculate the planar Z form to be 3.8 kcal/mol above planar E (Table III), corresponding to a Z:E ratio of 0.001 at 293 K, a ratio that is very sensitive to the energy difference. This theoretical result does not find support from experiment, as seen from Figure 6.

To explain the experimental spectrum in Figure 6, we clearly need the spectrum calculated for planar E. The strong band at 1134 cm⁻¹ has a FWHM of around 40 cm⁻¹, whereas weaker bands have FWHM of around 15 cm⁻¹. The 1134 cm⁻¹ band may thus arise from superposition of two to three individual bands and hence from the calculated spectrum, are compared with the spectral results in Figure 8.

One point should be made here. For planar E, the calculated 1550 cm⁻¹ band is of the same intensity as the calculated 1173 and 1158 cm⁻¹ bands together, and the sum of the y factors for the calculated planar E 1550 and planar Z 1537 and 1521 cm⁻¹ bands is less than twice the total y for the planar E 1173 and 1158 and planar Z 1115 cm⁻¹ bands. The observed 1560 cm⁻¹ bands, however, is 4 to 5 times stronger than the 1134 cm⁻¹ band. Hence, it appears that the QCFF/PI calculation underestimates the intensity of the band observed at 1560 cm⁻¹. A similar effect has been found also in studies of 1,3,5-hexatriene and DMHT.11,13 and leads to the conclusion that comparison of calculated and observed intensities should not include the band around 1550 cm⁻¹.

Although the remaining bands calculated for planar E all have experimental counterparts, it is clear that the spectrum calculated for planar E cannot account for all the observed bands, and we have to invoke the planar Z or P forms or both. In this situation it is obvious that the observed 1218 cm⁻¹ band should be assigned to the planar Z band at 1251 cm⁻¹, and the observed 1434, 1393, and 1353 cm⁻¹ bands to contributions from both planar E and Z. The tP1 1308 cm⁻¹ band only has a weak experimental counterpart, if any.

The experimental spectrum in Figure 6 is thus rather unambiguously assigned to a combination of the planar E and Z forms. The tP1 form does not contribute, and from comparison of the intensity of, in particular, the experimental bands at 1134 and 1218 cm⁻¹ with the calculated spectra, it appears that the contribution from the planar Z form is smaller than that from planar E. With similar RR conditions, we thus conclude that planar Z is at higher energy than planar E, although less than predicted by calculation (3.8 kcal/mol).

(E)-2-MHT-4-d. The changes in the T1 RR spectrum of (E)-2-MHT upon deuteration are seen by comparison of the experimental spectra of (E)-2-MHT (Figure 3A or Figure 6, Table II) and (E)-2-MHT-4-d (Figure 7, Table II). The changes above 1200 cm⁻¹ are small with respect to both frequencies and intensities. In contrast, below 1200 cm⁻¹ large changes are seen upon deuteration. The observed (E)-2-MHT shoulder at 1197 cm⁻¹, the intense (E)-2-MHT band at 1134 cm⁻¹ ascribed above to a superposition of at least two bands, and the weak (E)-2-MHT bands at 1000 and 942 cm⁻¹ are replaced in (E)-2-MHT-4-d by a number of bands of medium intensity at 1169, 1094, 1031, 954, 902, and 823 cm⁻¹.

The changes in the calculated spectra are seen by comparison of Figures 6 with 7 (or see Table VI). For the tEt form, the calculated 2-MHT 1173 cm⁻¹ (y value 0.14) band is replaced in 2-MHT-4-d by bands at 1221 (0.06), 1019 (0.03), and 911 cm⁻¹ (0.03). For the ZtZ form, the calculated 2-MHT 1329 cm⁻¹ (0.04) band is replaced in 2-MHT-4-d by bands at 1230 (0.03) and 1035 cm⁻¹ (0.03).

The most significant change in the experimental spectra is the disappearance of the intense band at 1134 cm⁻¹; this change is described by the calculation for the tEt form. The appearance of rather strong bands below 1100 cm⁻¹ is predicted by calculation for both the tEt and ZtZ forms. Direct comparison between calculated and observed spectra in Figure 7 indicates that the ZtZ form is present as well, since the observed spectrum cannot be accounted for by the calculated tEt spectrum alone. Thus, the conclusions reached for (E)-2-MHT are confirmed by the results for (E)-2-MHT-4-d in Figure 7: Both tEt and ZtZ species are present, but the tEt form is dominant.

(Z)-2-MHT. In the transient RR spectrum of (Z)-2-MHT we found a number of bands that are observed also in the spectrum of (E)-2-MHT and were ascribed to the tXt forms. The remaining bands observed for (Z)-2-MHT and not for (E)-2-MHT, are ascribed to triplet species populated from the ZtZ minor ground-state component of (Z)-2-MHT. These bands, obtained by subtracting the E from the Z spectrum, are compared with the theoretical results in Figure 8.

It is obvious at once that in order to explain the observed spectrum in Figure 8, we need to invoke the planar E geometry. The experimental bands at 1192, 1155, and 1122 cm⁻¹ are assigned to the ones calculated for planar E at 1231, 1188, and 1135 cm⁻¹, with a possible contribution from the Z band at 1121 cm⁻¹. The strong observed 1557 cm⁻¹ band is assigned to the planar E band at 1552 cm⁻¹, with a possible contribution from the Z bands at 1533 and 1520 cm⁻¹. Again, calculation underestimates the intensity of the 1550 cm⁻¹ band.

The observed spectrum cannot be interpreted by considering the planar E form alone. The observed 1346 and 1324 cm⁻¹ bands can only be explained by the Z or P forms or both. The Z form gives the best fit, with the calculated bands at 1343, 1322, and 1240 cm⁻¹ corresponding to the observed 1346, 1324, and 1265 cm⁻¹ bands. In this case, the Z 1121 cm⁻¹ band in combination with the planar E 1135 cm⁻¹ band predicts correctly the intensity of the observed 1122 cm⁻¹ band relative to the observed 1192 and 1155 cm⁻¹ bands. When calculated and observed relative intensities are compared, the tZt:tEt ratio may be somewhat larger than the ZtZ:tEt ratio discussed above. It should be noted that the ZtZ species is predicted to be about 30° twisted at the central
Steric Control of Excited-State Molecular Structure

CC bond. The good fit between calculated and observed spectra in Figure 8 supports the conclusions reached above about the NEER principle.

(E)-3-MHT and (Z)-3-MHT. The methyl group of (E)-3-MHT in Figure 1 is staggered with respect to the neighboring terminal CH2 hydrogen atom, and all calculations reported here apply to this geometry (A) of the methyl group. We also carried out calculations for a geometry (B) with the methyl group eclipsed with the CH2 hydrogen. The B geometry was found to be nearly isoenergetic with the A geometry, and the differences in electronic transitions and RR spectra calculated for the two geometries were small. For this reason, we report data on the A geometry only. The same observations apply to the A and B geometries of (Z)-3-MHT.

In agreement with the NEER principle, we observe identical T1, RR spectra from (E)-3-MHT and (Z)-3-MHT. To improve the signal to noise ratio, we add the spectra from the two compounds, and the sum spectrum is found in Figure 9, together with theoretical results. Calculation predicts the tZt geometry in T1 to be lower in energy than the tEt form (Table IV). This ordering is opposite to that of 2-MHT, and we shall now compare this finding with experiment.

The general appearance of the experimental spectrum in Figure 9 shows a very strong band at 1558 cm⁻¹, a number of weak bands, and a relatively strong band at 1274 cm⁻¹. The spectrum calculated for the tEt geometry in Figure 9 predicts the strong 1558 cm⁻¹ band and a number of weak bands, but it does not predict the strong 1274 cm⁻¹ band. Thus, it is not possible to ascribe the observed spectrum to the planar E geometry alone. The observed band at 1274 cm⁻¹ can only be assigned to the planar Z form, although the three bands at 1313, 1260, and 1201 cm⁻¹ calculated for planar Z are not observed separately. However, the 1274 cm⁻¹ band may contain contributions from more than one vibrational band.

Although it was mentioned above that the QCFT/PI calculation tends to underestimate the intensity of the strong observed band around 1550 cm⁻¹, it is not likely that the observed 1558 cm⁻¹ band can be explained alone by the 1544 cm⁻¹ band calculated for planar Z, and we have to invoke the planar E form as well, with a calculated band at 1547 cm⁻¹.

The remaining bands are of moderate intensity, both the observed and calculated ones, and the observed bands can all be assigned to bands calculated for the planar E and Z forms. What are the relative populations of the planar E and Z forms? We note that the intensity ratio of the 1274 cm⁻¹ band to the other observed bands is 10 or more (apart for the 1558 cm⁻¹ band). The calculated ratio for the two forms is 10, but the calculated ratio for the two forms is 10. Thus, in T1, the tZt form of 3-MHT must be at lower energy than the planar E form. The calculated energy difference of 0.5 kcal/mol corresponds to a population ratio of 1:0.42 for Z:E, in qualitative agreement with the observed spectra.

E. Decay Kinetics of the Triplet State. It was previously shown 1 that the decay of the T1 state of (E)-1,3,5-hexatriene (EHT) is an activated process which in the temperature region 296-183 K in methanol can be described by an Arrhenius equation with an activation energy (Eₐ) of 0.7 ± 0.2 kcal/mol and a frequency factor (A) of (1.6 ± 0.3) × 10⁷ s⁻¹. We have recently extended these measurements to (Z)-1,3,5-hexatriene (ZHT), (E)-2-Methyl-1,3,5-hexatriene ((E)-2-MHT), (Z)-3-Methyl-1,3,5-hexatriene ((Z)-3-MHT), and (E)-((E)-DMHT) and (Z)-2,5-Dimethyl-1,3,5-hexatriene ((Z)-DMHT)

<table>
<thead>
<tr>
<th>Eₐ (kcal/mol)</th>
<th>A (10⁻⁷ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EHT⁺</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>ZHT</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>(E)-2-MHT</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>(Z)-3-MHT</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>(E)-DMHT⁻</td>
<td>0.0 ± 0.1</td>
</tr>
<tr>
<td>(Z)-DMHT⁻</td>
<td>0.8 ± 0.2</td>
</tr>
</tbody>
</table>


Figure 10. Qualitative potential energy surface for rotation at the central CC bond in the T1 state of (A) (E)- and (Z)-1,3,5-hexatriene, (B) (Z)-2,5-dimethyl-1,3,5-hexatriene, (C) (E)-2,5-dimethyl-1,3,5-hexatriene, (D) (E)-2-methyl-1,3,5-hexatriene, and (E) (Z)-2-methyl-1,3,5-hexatriene. Activation energies are indicated in kcal/mol.

The present study further extends these measurements to (E)-2-MHT with Eₐ = 0.4 ± 0.1 kcal/mol and A = (1.4 ± 0.2) × 10⁷ s⁻¹ and (Z)-3-MHT with Eₐ = 0.8 ± 0.2 kcal/mol and A = (2.7 ± 0.6) × 10⁷ s⁻¹. These values were obtained from Figure 5, where data points at four temperatures ((E)-2-MHT, 293, 246, 213, and 188 K; (Z)-3-MHT, 292, 244, 212, and 187 K) were used to determine the Arrhenius parameters. The points do not follow straight lines exactly; at least in part this effect can be ascribed to the strong increase in the viscosity of methanol in the vicinity of the melting point. As mentioned above, the buildup of the hexatriene triplet was also influenced by viscosity at low temperature.

The activation energies (Eₐ) and frequency factors (A) of triplet decay found for EHT, ZHT, (E)-2-MHT, (Z)-3-MHT, (E)-DMHT, and (Z)-DMHT, are summarized in Table VII. T1 potential energy surfaces (PES) proposed for these compounds are illustrated in Figure 10, where the energy of the P state is determined from the activation energy for triplet decay. We shall now discuss the interpretation of first the activation energies, then the frequency factors.
We previously interpreted the observed $E_i$ for the decay of T$_1$
EHT as the energy difference between the planar forms on the T$_1$
PES and the perpendicular form, from where decay to the S$_0$
PES occurs. For DMHT we interpret the observations in the following way. The dominant conformer of ground-state (Z)-
DMHT is cZt.$^3$ The T$_1$ PES of (Z)-DMHT has a minimum at the
cEt geometry, a maximum at cZt, and a barrier, or a shallow
minimum superimposed on the barrier, at the cPt geometry.$^{13}$
The activation energy observed for T$_1$ (Z)-DMHT is thus the energy of the
cEt form relative to the cEt form. For (E)-DMHT the dominant ground-state conformer is tEt.$^4$ The T$_1$ PES of (E)-
DMHT has a maximum at the cEt geometry, whereas the tPt and
tEt forms are nearly isoenergetic.$^{13,15}$ Thus the methyl groups
raise the energy of the tEt T$_1$ form relative to the tPt geometry.
The activation energies found in the present study for the decay of T$_1$:
(E)-2-MHT and (Z)-3-MHT can now be interpreted. For
(Z)-3-MHT (tEt in S$_0$, tEt and tZt in T$_1$), the methyl group causes
little steric hindrance in T$_1$, and the tEt and tZt forms are nearly
isoenergetic. This is similar to the 1,3,5-hexatriene case, and the
activation energies are similar to those of EHT and ZHT. For
(E)-2-MHT (tEt in S$_0$, tEt and tZt in T$_1$), we expect an inter-
mediate case between HT and (E)-DMHT. The methyl group
of (E)-2-MHT raises the energy of the tEt T$_1$ form relative to the
tPt geometry, but not as much as for (E)-DMHT, and the activation
energy for decay of T$_1$ (E)-2-MHT is intermediate between EHT and E-DMHT.

The frequency factor ($A$) in the Arrhenius equation for the
decay of T$_1$ is close to 2.0 $\times 10^8$ s$^{-1}$ for EHT, ZHT, and (Z)-
DMHT; for (E)-2-MHT $A = 1.4 \times 10^7$ s$^{-1}$, for (E)-DMHT $A =
1.0 \times 10^7$ s$^{-1}$, and for (Z)-3-MHT $A = 2.7 \times 10^6$ s$^{-1}$. Thus it
seems that methyl substitution in the 2- and 5-positions leads to a
decrease in the frequency factor for tPt conformers, whereas
methyl substitution in the 3-position leads to an increase. We
interpret the frequency factor as the rate constant for the spin-
forbidden intersystem crossing process from T$_1$ to S$_0$. The rate
of this process may be determined by several factors, e.g., the
energy gap at the perpendicular geometry between the T$_1$ and S$_0$
states, the size of spin-orbit coupling, and the density of states
on the T$_1$ and S$_0$ PES. The data now available do not allow one
to assess which factor is predominantly affected by methyl substi-
tution.

F. Comparison of 2-MHT and 3-MHT. Steric Control of
Excited-State Molecular Structure. For 2-MHT, calculation
placed the tEt form at 3.8 kcal/mol below tZt in the T$_1$ state.
From the comparison of calculated and observed RR spectra,
tEt form was found to be below tZt, but less than predicted by
theory. The discrepancy is readily explained by the tendency of
QCFF/PI to overestimate the steric hindrance in connection with
a methyl group. The results were confirmed by the results for
2-MHT-4-d. For the cEt forms of 2-MHT, calculation placed
cEt at 3.8 kcal/mol below cZt. Comparison between theory and
experiment again showed the same order, but seemed to indicate
that the energy difference was less than that for tEt and tZt. For
3-MHT, calculation placed the two T$_1$ forms close in energy, with
the tZt form lowest. This result was confirmed by comparison of
theoretical and observed spectra.

These findings lead to the following picture. In the T$_1$ state of
1,3,5-hexatrienes, equilibration with respect to torsion around
theoretical CC bond is very fast between the planar E and Z forms.
The energy of the P form is not exactly determined, but it is
probably above the planar forms in energy.$^{12}$ Different rotamers
around the C$_4$C$_5$ and C$_5$C$_6$ bonds do not equilibrate in the T$_1$
state, in agreement with the NEER principle. For unsubstituted
1,3,5-hexatriene, the planar E and Z T$_1$ forms are nearly iso-
energetic. For methyl-1,3,5-hexatrienes, the distribution between
the planar E and Z forms is largely determined by steric hindrance.
For 2,5-dimethyl-1,3,5-hexatriene, the Z form is pushed to higher
energy, such that only planar E is populated.$^{13}$ For 2-MHT, tEt
is lower in energy than tZt, but both forms are populated; tEt
is also lower than cZt, but their energies are closer than in the
tt conformer. For 3-MHT, the planar Z form is slightly lower
in energy than the planar E form.

In the ground state of 1,3,5-hexatrienes, the steric hindrance of
the methyl groups is relieved by rotation around the C-C single
bonds. In the T$_1$ state, the steric hindrance induces a torsion
around the central CC bond. Thus, steric interactions can govern
the change in geometry upon excitation and the geometry of the
excited state itself. This may be of consequence on the photo-
chemistry ensuing the decay of the excited state.

VI. Conclusions

The analysis of transient T$_1$ RR spectra of 2-MHT and 3-MHT
allows an assignment of the observed spectra to the E and Z species
which equilibrate during the T$_1$ lifetime. This observation, which
applies also to HT$^{12}$ and DMHT,$^{13}$ is explained by admitting that
the potential energy curve for the torsion around the central C-C
bond is essentially flat.

The comparison of the spectra of (Z)-MHT with the spectra
of (E)-MHT indicates that the t$^t$, t$^c$, and c$c$ rotamers do not
equilibrate in the T$_1$ state but remain at their ground-state dis-
tribution. This result, which has already been found for DMHT,$^{13}$
implies that the NEER principle is valid also for the T$_1$ state of
1,3,5-hexatrienes and is related to the high barrier encountered
in the rotation around the formal C-C single bonds in T$_1$.

The relative intensities of the observed bands attributed to
the E and Z forms, compared with the theoretical intensities, provide
information about the relative energy of the E and Z forms. This
allows a qualitative knowledge of the energy effects of methyl
substitution. It is found that changing the position of the substi-
tution and the number of substituents can change the shape of the
T$_1$ potential energy curve for the torsion around the central
CC bond and the distribution of conformers in S$_0$ and therefore in
T$_1$. These effects are important because they may alter the
efficiency of the possible photochemical processes taking place in
T$_1$. They are of relevance also in understanding the role of
methyl groups that are found in many natural chromophores of
the polynye type.$^{21}$

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Registry No. (E)-2-MHT, 41233-72-1; (E)-2-MHT-4-d, 124886-99-
3; (Z)-2-MHT, 26502-11-4; (E)-3-MHT, 24587-26-6; (Z)-3-MHT,
24587-27-7; HT, 2235-12-3; DMHT, 4916-63-6.

Supplementary Material Available: Computed geometries in the
S$_0$, T$_1$, and T$_2$ states and wavenumbers and Stokes shift pa-
rameters $\gamma$ of totally symmetric normal modes in the T$_1$
state for the isomers and rotamers of 2-MHT, 2-MHT-4-d, and 3-MHT
(10 pages). Ordering information is given on any current masthead page.