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Lowest Excited Triplet State of 2,5-Dimethyl-1,3,5-hexatriene: Resonance Raman Spectra and Quantum Chemical Calculations

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Theoretical and Raman spectroscopic studies are presented of the ground and lowest excited triplet states of (E)- and (Z)-2,5-dimethyl-1,3,5-hexatriene and their 3,4-dideutero and 3-deutero isotopomers. The T1 potential energy surface is calculated from SCF-LCAO-MO-Cl theory. Energy minima and equilibrium geometries are determined in the T1 state. Frequencies and normal modes of vibrations are calculated for the minima of the T1 and S1 states. The types of high to inter- levels are computed and oscillator strengths for the T1 → T1 transitions are determined. The displacements in equilibrium geometries between the T1 and the T1 level corresponding to the strongest T1 → T1 transition are calculated and are used to estimate the intensities of the resonance Raman spectra of the T1 state under the assumption of a predominant Franck-Condon scattering mechanism. The influence of the ground-state conformation around C-C single bonds on T1 resonance Raman spectral sensitivity is considered in detail for the two isomers. It is found that for the E isomers the T1Z and for the Z isomers the T1E forms are the predominant ones in the T1 state. The Z forms are at considerably higher energy than the E forms in the T1 state due to nonbonded interaction. A good agreement is found between theoretically calculated and experimental spectra. The results are compared with previously published data for 1,3,5-hexatriene.

Introduction

In previous studies1-3 we considered the transient resonance Raman (TRR) spectra of 1,3,5-hexatriene (HT) in its T1 state with the purpose of obtaining information about the geometry of the T1 intermediate and about the mechanism of the cis-trans photoisomerization in T1. The experimental TRR spectra, which have been found to be identical in experiments on solutions of either of the two ground-state isomers, were interpreted by quantum mechanical calculations of equilibrium geometries and vibrational frequencies at the trans (E), cis (Z), and centrally twisted (P) geometries in T1 and in the T1 state responsible for the TRR activity. On the basis of these calculations the T1 normal modes showing the strongest Franck-Condon activity in the TRR spectra could be identified for each geometric isomer of HT. The observed TRR spectra were shown to be due to a superposition of the spectra of the Z, E, and P forms with possible weak contributions from the P form. It was concluded that the transient T1 intermediate in the photoisomerization of HT, monitored by TRR spectra, consists of an equilibrium between several geometric structures, in which planar molecules represent a small fraction, and that a possible minimum of the potential energy curve at the centrally twisted geometry must be rather shallow.

In this paper we consider the TRR spectra of the T1 intermediate of the 2,5-dimethyl derivative of HT, 2,5-dimethyl-1,3,5-hexatriene (DMHT). Due to the presence of two CH3 groups and to the steric strain associated with them, we may expect modifications of the electronic potential energy surfaces (PES) compared with HT. In particular, the potential energy curve for cis-trans photoisomerization of DMHT could be different from that of HT. In addition, the different trans-cis (t-c) conformers with respect to the two CC single bonds could be roughly isoelectronic in DMHT, due to similar nonbonded interactions of CH3 and —CH2 groups, and this may lead to the presence of several additional species that need to be considered in the calculations. Experimentally, it has been found for the ground state that the E form corresponds to only one conformer, namely tEt, while the Z form is associated predominantly with the tZc conformer with a minor fraction of the ZcE conformer.4 Figure 1 shows a planar representation of the six possible ground-state geometries of DMHT. In reality, some of the forms are nonplanar.

The T1 TRR spectra of the two isomers of nondeuteriated DMHT have been reported previously.5 The spectra of (E)- and (Z)-DMHT-3,4-d2 and of (E)-DMHT-3-d are reported in the present paper together with remeasured spectra of DMHT-d6. The experimental TRR spectra of (E)- and (Z)-2,5-DMHT have been found to be different.6 This is reasonable since in T1 the CC "single" bonds become shorter, and consequently, the barrier for rotation becomes too high for the molecule to be able to interconvert among the different conformers during the T1 lifetime (~80–170 ns). In other words, the principle of nonequilibrium of excited rotamers (NEER) previously formulated for excited singlet states6 is valid also for the longer lived T1 states of DMHT.

with the experimental spectrum; as we shall see, the comparison of the transition and for the TRR activity. The Franck-Condon (FC) activity of each totally symmetric vibration in the TRR spectra of deuteriated isotopomers of 2,5-DMHT using the same procedure indicates unambiguously which of the E, Z, and P forms of the conformer(s) dominant in the S0 state.

We here analyze the TRR spectra of nondeuteriated and some deuteriated isotopomers of 2,5-DMHT using the same procedure as in ref 2. That is, we compute the T1 vibrational frequencies of the E, Z, and P isomers, not only for the t,t conformer (as done for HT), but also for the t,c and c,c conformers, and we identify the excited T1 state that is responsible for the strongest T1 → T0 transition and for the TRR activity. The Franck-Condon (FC) activity of each totally symmetric vibration in the TRR spectra of the TI state in TI is computed for each isomer and conformer and is compared with the experimental spectrum; as we shall see, the comparison indicates unambiguously which species give the largest contribution to the spectrum.

Experimental Methods

Materials. Acetonitrile-d6 (Merck, LiChrosolv), acetonitrile-d4 (Stohler Isotope Chemicals, 99% D), methanol (Merck, p.a.), and acetone (Merck, p.a.) were used as received. The deuterium DMHT was prepared as described in refs 4a and 8. The deuterium incorporation was better than 95%. Throughout the transient experiments the capillaries with trienes were opened and the atmosphere. Prior to the addition of triene the solvents were purged with Ar for more than 35 min.

Methods. The details of experimental procedures for recording conventional Raman and infrared spectra8 and for time-resolved experiments13 have been described previously. Briefly, the triplet state of the triene was produced by exciting acetone as sensitizer at the second harmonic at 327.5 nm from a pumped dye laser as probe pulse. The triplet-state spectra were computed by means of the QCFF/PI Hamiltonian, which has been successfully used to predict a variety of properties of ground and excited states of conjugated molecules.11-13 This method was used in the modified form outlined in refs 2 and 14. Energies and wave functions of triplet levels were computed by using both the QCFF/PI and the CNDO/Cl5 Hamiltonians. In the latter case the electron repulsion was computed according to the Pariser relation.16 The transition dipole moments for the T1 → T0 transitions were also computed by both methods.

Ground-state calculations were performed at the SCF level, while all calculations on triplet states were performed by the half-electron SCF Hamiltonian followed by a configuration interaction (CI) calculation in which all singly excited determinants with respect to the lowest triplet, belonging to the π-π* space, were considered. This CI included 33 π-π* determinants with two unpaired spin α electrons.

In the present QCFF/PI calculations we introduced a different set of parameters for C–CH3 bonds, between an sp2-hybridized carbon and an sp3-hybridized methyl carbon (AB bonds, as in, for example, propene). The potential for the stretching of these types of bonds is described by the equation

\[ V = \frac{1}{2} k_0 (b - b_0)^2 - D_0 \]

The original parameters \( \frac{1}{2} k_0 = 250 \text{ kcal mol}^{-1} \text{ Å}^{-2}, b_0 = 1.450 \text{ Å}, \text{ and } D_0 = 88 \text{ kcal mol}^{-1} \) have been replaced by the values \( \frac{1}{2} k_0 = 150 \text{ kcal mol}^{-1} \text{ Å}^{-2}, b_0 = 1.427 \text{ Å}, \text{ and } D_0 = 88 \text{ kcal mol}^{-1} \). This modification is justified by the fact that for all methylated polyenes the previous parameters yield too high C=CH2 stretching frequencies, in particular for compounds that contain two methyl groups on the same carbon atom or one methyl group adjacent to a C=C single bond of a polyenic chain. This set of parameters was used with success in the study of 2,5-dimethyl-2,4-hexadiene.17

Vibrational frequencies and normal coordinates were computed at the E and Z geometry minima of S0 and T1 and at the twisted geometry of T1, i.e., the geometry obtained by twisting the central C=C bond by 90°. All the computed frequencies are adiabatic frequencies, that is, they are obtained with the energy hessian computed by also taking into account the contribution of electron density change (see ref 14).

The displacements in equilibrium geometry between the T1 and T0 states correspond to the strongest T1 → T0 transition for each geometry were calculated and were used to calculate the Stokes shift parameter \( \gamma_1 \) of each totally symmetric normal mode. The \( \gamma_1 \) parameter, which governs the contribution to the resonance Raman spectrum of the ith displaced oscillator, under the condition of a predominantly Franck-Condon mechanism, is given by

\[ \gamma_1 = (\omega_i/2h)\Delta Q^2 \]


Figure 1. Planar ground-state forms of DMHT.

Figure 2. Numbering of atoms in DMHT.
Figure 3. Ground-state Raman spectra of (A) (E)-DMHT-3,4-d$_2$ and (B) (E)-DMHT-3-d. Excitation: (A) 514.5 nm, (B) 327.5 nm.

where $\omega_i$ is the vibrational frequency (rad s$^{-1}$) and $\Delta Q_i$ is the projection onto the $i$th normal coordinate of T$_1$ of the change in harmonic, have a clear physical meaning only for small distortions, the potentials of which are intrinsically anharmonic, have a clear physical meaning only for small displacements $\Delta Q_i$ that is when the $\gamma$'s themselves are small ($\lesssim$0.5).

The numbering of atoms for 2,5-DMHT is shown in Figure 2. The torsional angles of the two methyl groups were such that these molecules in the planar form belong to the C$_{2h}$ symmetry group (Figure 2).

Results and Discussion

Experimental Results. (a) Ground State. The ground-state Raman and infrared spectra of (E)-DMHT have been reported previously. The Raman spectrum of neat (E)-DMHT-3,4-d$_2$, excited at 514.5 nm (CW excitation), is shown in Figure 3A and the corresponding resonance Raman spectrum of an Ar-saturated solution of 0.007 M (E)-DMHT-3-d in acetonitrile-d$_3$ containing 0.54 M acetone, excited at 327.5 nm (pulsed excitation), is seen in Figure 3B. The frequencies of the observed Raman and infrared bands are listed together with results from the theoretical calculations in Table V.

(b) Triplet State. The excited state Raman spectra of the E isomers of DMHT, DMHT-3,4-d$_2$, and DMHT-3-d in the T$_1$ state are shown in Figure 4 and those of the Z isomers of DMHT and DMHT-3,4-d$_2$ in Figure 5. The corresponding wavenumbers are tabulated together with calculated bands in Tables IX–XI.

The spectra were obtained from the following Ar-saturated solutions: (1) 0.010 M (E)-DMHT in methanol and 0.82 M acetone, (2) 0.007 M (E)-DMHT-3,4-d$_2$ in acetonitrile-d$_3$ and 0.54 M acetone, (3) 0.007 M (E)-DMHT-3-d in acetonitrile-d$_3$ and 0.54 M acetone, (4) 0.001 M (Z)-DMHT in methanol and 0.82 M acetone, (5) 0.004 M (Z)-DMHT-3,4-d$_2$ in acetonitrile-d$_3$ and 0.54 M acetone. The excitation wavelength was 327.5 nm, and the delay between pump and probe pulses was approximately 60 ns in all transient experiments. All spectra shown in Figures 4 and 5 are spectra after the subtraction of solvent bands and bands from ground-state DMHT, obtained by procedures described in detail previously. Such subtraction procedures can produce artifacts showing up as either negative bands due to the wavelength dependence of transient absorption and to depletion and/or combination of the starting ground-state isomer or as positive bands due to isomerization products. All spectra were carefully examined for such artifacts and the bands listed in Tables IX–XI are considered as real. Outside the regions shown in Figures 4 and 5, spectra were recorded down to 200 cm$^{-1}$ and some weak observed bands are listed in the tables as well.

Figure 6 shows a detailed comparison of the spectra obtained from the E and Z isomers of DMHT-d$_0$ and DMHT-d$_2$. From this it is obvious that the spectra from the two isomers are different from each other.

The isomeric purity of the samples was monitored by gas chromatography throughout the experiments. We observed thermal isomerization of (Z)-DMHT in methanol solutions containing acetone to 1,4-dimethyl-1,3-cyclohexadiene upon storage under Ar for several days at room temperature.

Theoretical Calculations and Discussion. (a) T$_1$ and T$_2$, Triplet States. Energies and wave functions of the triplet states of HT are given in Tables XVI–XVIII of ref 2. Since the $\pi$-electron system is the same, the nature of the triplet states in DMHT is practically the same as in HT. The lowest triplet state T$_1$ is dominated by the (HOMO–LUMO) singly excited configuration. The excited triplet state T$_2$, characterized by the largest transition moment $M(T_2)$, is TS in both E and Z isomers: this state lies ~4.2 eV above T$_1$ and is dominated by the (HOMO–LUMO) and (HOMO → LUMO + 1) configurations. At the twisted geometry the state with the largest $M(T_2)$ transition moment is T$_6$, T$_7$, or T$_8$ (depending on the rotamer) and lies 5.5 eV above T$_1$.

The excitation wavelength used in the TRR experiments to be discussed is $\lambda = 327.5$ nm, which corresponds closely to the T$_5$–T$_1$ energy gap in the E and Z species. Thus it is the T$_5$ state, or the T$_5$ state (n = 6, 7, 8) state at the twisted geometry, that is responsible for the TRR scattering and that is to be scrutinized to interpret the observed TRR spectra. It is worth noting also that while the intense T$_5$–T$_1$ transition of the E and Z forms is in resonance with the exciting photons, the correlating transition is off-resonance by ~1 eV at the P geometry.

(b) Optimized Geometries and Energies. The energies of the different isomers of DMHT in their optimized geometries in the states $S_0$, T$_1$, and T$_2$ are shown in Table I. The $T_1$ and T$_2$ states are calculated to be the most stable in the three electronic states. The conformers of the E isomer ($tEt$, $tEe$, and $cEc$) are found to be almost degenerate, as their energies differ by less than 1 kcal/mol. However, the computed energies of the conformers in the ground state are not in the correct order: the calculations predict that $cEc$ is the most stable conformer, while experimentally, $tEt$ is the dominant one. A similar inversion of stability is also found between the $tZc$ and $cZc$ conformers in $S_0$: at variance with our results, $tZc$ is found experimentally to be the most stable conformer.

In Tables II–IV the geometric parameters of the carbon atom backbone are given for the three states $S_0$, T$_1$, and T$_2$ of DMHT, respectively. These results are very similar to the results obtained earlier for HT: the main differences pertain to the in-plane angle $C_4C_5C_6$, which is larger here due to steric hindrance, and to the dihedral angles $C_2C_3C_4C_5$ and $C_2C_3C_6C_7$ of the Z isomer, which are nonplanar in DMHT. The CC bond lengths are almost identical in the different conformers. In contrast to this, the in-plane CCC angles depend on the type of isomer; in particular,
Figure 4. $T_1$ resonance Raman spectra of the $E$ isomers of DMHT-d$_0$ (left), DMHT-3,4-d$_2$ (center) and DMHT-3-d$_1$ (right). (A) calculated spectra for the $tE^-$ geometry in resonance with the $T_1 \rightarrow T_5$ transition; (B and C) experimental spectra, excitation wavelength 327.5 nm, after the subtraction of solvent and ground-state bands.

Figure 5. $T_1$ resonance Raman spectra of the $Z$ isomers of DMHT-d$_0$ (left) and DMHT-3,4-d$_2$ (right). (A) Calculated spectra for the $tE^-$ geometry in resonance with the $T_1 \rightarrow T_5$ transition; (B and C) experimental spectra, excitation wavelength 327.5 nm, after the subtraction of solvent and ground-state bands.

Figure 6. Comparison of the $T_1$ resonance Raman spectra of the $E$ and $Z$ isomers of DMHT-d$_0$ (left) and DMHT-3,4-d$_2$ (right). Conditions as for Figures 4 and 5.

Table II: Ground-State Geometries for the Various Isomers of 2,5-DMHT$^*$

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<tr>
<th>Isomer</th>
<th>$tE^-$</th>
<th>$tE^c$</th>
<th>$tZ^-$</th>
<th>$tZ^c$</th>
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<td>1.349</td>
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<tr>
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<td>1.357</td>
<td>1.356</td>
<td>1.356</td>
</tr>
<tr>
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<tr>
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<td>1.500</td>
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<tr>
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<td>1.500</td>
<td>1.488</td>
<td>1.501</td>
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<tr>
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<td>123.4</td>
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<td>123.4</td>
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<td>358.3</td>
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<td>174.2</td>
</tr>
</tbody>
</table>

$^*$Bond lengths in Å; bond angles in degrees.

TABLE II: Ground-State Geometries for the Various Isomers of 2,5-DMHT

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in the $Z$ isomer these angles show deviations of up to 15° (especially in the ground state) with respect to the customary 120° value. Furthermore, while the $E$ isomers are close to planar, the $Z$ isomers are nonplanar. In the ground state torsion takes place predominantly around the CC single bonds, in the $T_1$ state predominantly around the central CC bond.

As in HT, the main differences caused by electronic excitation pertain to the CC bond lengths. In $S_0$ the CC bond lengths show the well-known alternation according to the single/double bond character of adjacent bonds. These results are in good agreement with the parameters obtained by electron diffraction. Upon $S_0 \rightarrow T_1$ excitation, the double bonds lengthen and single bonds shorten, as found in the previous studies of HT. In $T_1$ the CC bond lengths are intermediate between the values taken in $S_0$ and in $T_1$.

(c) Ground-State Vibrational Frequencies. In Table V we present the computed vibrational frequencies and the approximated description of the normal coordinates of DMHT and of its $d_1$ and $d_2$ isotopomers in the experimentally most stable conformer $tE^-$ of $S_0$. The experimental frequencies of DMHT-d$_0$ have been recently studied and assigned by Langkilde et al.\textsuperscript{16} A few assignments of the weakest bands are revised here, in part on the

basis of a comparison with (E)-2-methyl-1,3,5-hexatriene and (E)-4-deuterio-2-methyl-1,3,5-hexatriene. The agreement between computed and observed in-plane frequencies is quite satisfactory. In particular, the present calculations confirm the coupling between the polyenic C-C single bond stretch and the C-CH3 stretch vibration, suggested by Langkilde et al.18 which leads to a repulsion between the two frequencies. It is worth noting that the updating of the parameters describing the C-CH3 potential, discussed above, is instrumental in improving the agreement between the experimental and theoretical frequencies of C-CH3 vibrations.

The list of the experimental out-of-plane frequencies is not complete, mainly because the low-frequency (below 530 cm⁻¹) range was not explored by IR spectroscopy. The agreement between computed and observed out-of-plane frequencies is satisfactory.

(d) T1 Vibrational Frequencies. In Table VI we report the T1 frequencies of the d3, d1, and d2 isotopomers of the tEt conformer. The S0 → T1 excitation affects mainly the force field of the C=C and C=C stretches and torsions. Thus, most of the differences between the T1 and S0 frequencies are noted in the range 1100 cm⁻¹. At the same time, normal coordinates, especially for modes of CC character, undergo a mixing (Duschinsky effect) when passing from S0 to T1. Comparing the T1 frequencies of DMHT with those of the parent molecule HT, we note that most frequencies of the latter show up virtually unchanged also in DMHT, where they are intermingled with the frequencies pertinent to the CH3 groups.

In Table VI we report also the γ parameters that were defined above. Since these parameters are proportional to the Franck-Condon intensity of the corresponding fundamentals in the TRR spectra, they are essential for the interpretation of these spectra. The modes with nonzero γ are the aγ modes and the largest γ values are associated with the vibrations at 1545, 1173, and 304 cm⁻¹ in DMHT-d6. Hence, as it might have been anticipated, the computed γ are quite similar to the γ found for HT. The effect of deuteration is that of introducing some redistribution among the γ parameters as a consequence of the normal coordinate mixing.

In Tables VII and VIII we show the T1 frequencies and the γ parameters for the T1 → T1 transition of the conformers tEc and tEc in the isotopomers d3 and d2. The changes in the list of the frequencies compared with those of the tEt conformer are rather small; however, modifications are found in the normal coordinates and these are reflected in the values of the γ's, especially for the frequencies in the region around 1100 cm⁻¹. The results for the Ec conformer show a further difference with respect to the tEt conformer because in tEc the center of symmetry is lost, the distinction between the g and u symmetry labels becomes meaningless, and thus, vibrations of bγ parentage (at 1278 and 941 cm⁻¹) may acquire intensity.

The full list of frequencies and γ parameters of the tZ1, tZc, cZc, tP1, tPc, and cPc forms are not reported here, but are available as supplementary material. In the next section, those frequencies with the largest γ's will be reported and discussed.

(e) Comparison between Computed and Observed Spectra. In this section we compare the frequencies and the intensities of the bands appearing in the TRR spectra with the computed frequencies and the γ parameters of T1 normal vibrations of each conformer for the three E, Z, and P isomers. The availability of deuteriated isotopomers adds more strength to the proposed assignments.
According to the NEER principle, ground-state conformations at C–C single bonds are preserved upon excitation to the excited T1 state. On this basis the dominant ground-state tEr conformer barrier (>8 kcal/mol for DMHT5) of the rotation around C–C isomer is rEt, while the dominant rEr, rPt, and rZr conformers are identical and this agrees with the notion that also in TI the dominant ground-state conformer tZc is the same in each geometric isomer. In Table IX we compare the experimental T1 spectrum of the d0, d1, and d2 isotopomers of the E isomer with the theoretical results for the tEt, tPt, and tZr conformers of the same species. We recall that the tZr conformer is computed to be 7.1 kcal/mol higher in energy than tEt and thus it is not expected to contribute significantly to the TRR spectra of the E isomer of DMHT. Furthermore, the tPt species is calculated to be off-resonance by ~1 eV with respect to the excitation wavelength.

The T1 spectrum of (E)-DMHT-d2 is composed of two intense bands at 1551 and 1146 cm\(^{-1}\) and weak bands at 1389, 1357, 1266, 1082, 1060, 1019, and 916 cm\(^{-1}\). The spectrum computed for tEt corresponds well to the observed spectrum, although the calculated intensity of the band at 1335 cm\(^{-1}\) is too low. We note that for this geometry a band of medium intensity is calculated at 304 cm\(^{-1}\). This band was indeed observed at 360 cm\(^{-1}\) in experiments performed at 188 K (not reported here). The spectrum computed for tPt does not match even the main features of the observed spectrum. The spectrum calculated for tZr predicts correctly the main observed bands, but it also predicts very strong bands at 462, 321, and 260 cm\(^{-1}\), which are not observed experimentally.

The observed T1 spectrum of (E)-DMHT-d2 differs from the spectrum of the nondeuteriated species in that the intense band at 1317 cm\(^{-1}\) is too low. We note that for this geometry a band of medium intensity is calculated at 304 cm\(^{-1}\). This band was indeed observed at 360 cm\(^{-1}\) in experiments performed at 188 K (not reported here). The spectrum computed for tPt does not match even the main features of the observed spectrum. The spectrum calculated for tZr predicts correctly the main observed bands, but it also predicts very strong bands at 462, 321, and 260 cm\(^{-1}\), which are not observed experimentally.

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at 1146 cm\(^{-1}\) is replaced by four medium-intensity bands at 1195, 994, 958, and 945 cm\(^{-1}\). The spectrum computed for \(tEc\) corresponds closely to the observed spectrum since it reproduces the intense band at 1519 cm\(^{-1}\) and the intensity redistribution in the region 1200–900 cm\(^{-1}\). The spectrum computed for the \(tPt\) species does not match the observed spectrum because the band calculated at 1389 cm\(^{-1}\) comes out too strong, as intense as the calculated 994, 958, and 945 cm\(^{-1}\). The spectrum computed for the \(tPt\) species overestimates the intensity and the number of bands in the 1400-cm\(^{-1}\) frequency region. The spectrum computed for the \(tZt\) species lacks the counterpart of the band observed at 1354 cm\(^{-1}\) and overestimates the intensity of the 1154-cm\(^{-1}\) band. Moreover, strong calculated bands for \(tZt\) at 436, 311, and 255 cm\(^{-1}\) are not observed experimentally.

It follows that the TRR spectra of the three isotopomers of (E)-DMHT species are well represented by the spectra computed for the \(tE\) conformer, whereas the spectra computed for the \(tPt\) and \(tZt\) conformers cannot be reconciled with the observed spectra. The calculated \(tE\) spectra of the three isotopomers of (E)-DMHT are shown in Figure 4 together with the corresponding experimental spectra.

The \(T_{1}\) spectra of the \(d_0\) and \(d_1\) isotopomers of the (Z)-DMHT species are compared in Table X with the theoretical results obtained for the \(tE\), \(tP\), and \(tZt\) conformers of the same isotopomers and in Table XI with the results pertaining to the \(cEc\), \(cPc\), and \(cZc\) conformers. We recall that, experimentally, the \(tZt\) conformer is more stable than the \(cZc\) conformer in \(S_0\) and then,
on the basis of the NEER principle, the tEc conformers are expected to be the species that contribute most to the observed TRR spectra originating in T1.

The T1 spectrum of the (Z)-DMHT-d2 species is formed by two intense bands at 1548 and 1151 cm⁻¹ and by weak bands at 1392, 1350, 1320, 1252, 1004, and 927 cm⁻¹. The intensity computed for the modes of the tEc conformer represents quite satisfactorily the observed spectrum. The spectrum computed for the tEc species lacks the intensity band at 1151 cm⁻¹ and underestimates the intensity of the CC stretch at 1548 cm⁻¹. The spectrum computed for the tEc rotamer is slightly better, but here, the intensity associated to the 1548-cm⁻¹ band is split among a number of modes, and strong calculated bands at 469 and 315 cm⁻¹ are not observed experimentally.

The calculation of the cEc conformers leads to TRR spectra that are less satisfactory than the spectra obtained for tEc conformers. In particular, these spectra do not represent correctly the observations in the range 900-1200 cm⁻¹.

The T1 spectra of (Z)·DMHT-d2 are composed of an intense band at 1519 cm⁻¹ and of a number of medium-intensity bands at 1195, 1000, and 960/949 cm⁻¹. The spectrum computed for the tEc conformer represents rather well the observed spectrum. The spectra computed for the other two isomers, tPc and tZc, are substantially different from the experimental spectrum, as it can be seen in Table X. Among the cEc conformers, only the spectrum for the cEc species reproduces reasonably well the TRR spectrum of (Z)-DMHT-d2.

It follows that the T1 spectra of the d0 and d2 isotopomers of (Z)-DMHT are represented satisfactorily only by calculations for the tEc species. Theoretical spectra for the P and Z isomers are clearly less satisfactory; furthermore, TRR spectra are reproduced better by calculation on the tEc than on the cEc conformer. This fact agrees with the observation that in S0, the Z form exists predominantly as the tEc conformer. The calculated tEc spectra are shown in Figure 5 together with the experimental spectra of the Z isomers of DMHT-d0 and DMHT-d2.

As the previously reported T1 spectra of (E)· and (Z)·DMHT showed rather small differences they were remeasured in methanol in the present work. In Figure 6 characteristic regions of the spectra of the two isomers of DMHT-d0 and DMHT-d2 are shown. From Figure 6 it is seen clearly that differences are observed in the T1 spectra of the two isomers from both isotopomers, in particular with respect to intensities but also to frequencies. Having assigned the observed TRR spectra of (E)·DMHT and (Z)·DMHT to the tEc and tEc species, respectively, we now give a qualitative description of the normal modes that contribute most to the spectra. The intense bands at 1520-1550 cm⁻¹ can be assigned to a combination of C=C and C-C stretches, as shown in Tables VI and VII. Their intensity can be explained in terms of the large CC bond length change between T1 and Tm. The other
strong band, at ca. 1150 cm\(^{-1}\) in nondeuterated compounds, is assigned to the central \(\text{C} = \text{C}\) stretch; its frequency is considerably lowered with respect to the ground state because of its decreased bond order upon \(S_0 \rightarrow T_1\) excitation and its intensity is due to the change in the bond length observed in the \(T_1 \rightarrow T_0\) excitation. Deuteriation leaves the higher frequency band unaltered, but splits the lower frequency band into a number of bands: this observation is understood as due to the mixing of the central \(\text{C} = \text{C}\) stretch with CD rocks with the effect of pushing the frequency with dominant \(\text{C} = \text{C}\) character up to ca. 1200 cm\(^{-1}\).

We shall now discuss the reasons why the \(E\) isomer is the only one responsible for the \(T_1, \text{TRR}\) spectra. The absence of contributions from the \(Z\) isomer is attributed to its negligible population in the equilibrium \(T_1\) triplet, due to its relatively high steric energy and to the freedom of the molecule to rotate around the central \(\text{C} = \text{C}\) bond. The lack of indications of the \(P\) form in the TRR spectra cannot be attributed simply to its low population. First of all, the energy of the \(P\) form is similar to, and according to some calculations even lower than, the energy of \(E\) isomer. (As discussed previously,\(^{17}\) QCFF/IP tends to overestimate energies of twisted geometries.) Furthermore, there is at least a second reason for the lack of bands attributable to the \(P\) isomer: as discussed above, RR scattering in the experiments discussed is of preresonance (PR) character in the \(P\) form, but of resonance type in the \(E\) or \(Z\) form. The photon energy of the probing light used in these experiments matches the \(T_1 - T_0\) energy gap in the planar forms, but is lower than the computed \(T_1 - T_0\) energy gap of the intense triplet–triplet transition in the \(P\) form.\(^{23}\)

In the following, we estimate the ratio between the Raman scattering efficiencies of the \(E\) and \(P\) forms in order to assess their population ratio from the observed spectra. We consider for simplicity a model based on a single mode. The intensity of the PR Raman effect is\(^{20}\)

\[
I_{PR} = 4M_{I_n}^2\omega^2\gamma^2(E_{1_n}^2 + \Omega^2 + E_{I_n}^2)\]

where \(\gamma\) is the displacement parameter of the active mode, \(\omega\) is its frequency, \(M_{I_n}\) and \(E_{I_n}\) are the transition moment and the energy difference, respectively, between \(T_1\) and \(T_0\) triplets, and \(\Omega\) is the exciting photon energy.

The intensity of RR scattering, when the exciting photons are in resonance with the 0-0 band of \(T_1 \rightarrow T_0\) transition is\(^{20}\)

\[
I_{RR} = \frac{(\omega^2 + 2\Omega^2)M_{I_0}^4}{E_{I_0}^2 - \Omega^2}
\]

where \(\Gamma\) is the homogeneous line width of the 0-0 band.

In the \(T_1\) spectra of DMHT, the scattering of planar molecules is in-resonance and that of twisted molecules is off-resonance by ca. 1 eV, as can be deduced from the \(T_1 - T_0\) excitation energies at different geometries (vide supra). The transition moments are roughly the same in the two cases\(^2\) and this holds also for the \(\gamma\) parameter of the most active mode. Thus the model parameters we adopt are as follows: \(E_{I_0} = 32000\text{ cm}^{-1}\) (in resonance), \(\Omega = 32000\text{ cm}^{-1}, E_{I_0} = 40000\text{ cm}^{-1}\) (preresonance), \(\gamma = 1.0, \omega = 16000\text{ cm}^{-1}, \Gamma = 300\text{ cm}^{-1}\). \(M_{I_0}\) is taken to be the same for both RR and PR scattering. With these parameters we get a ratio of scattering intensities \(I_{PR}/I_{RR} = 2000\). Thus, with the laser excitation wavelength used, the scattering activity of \(E\) isomers is \(\sim 2000\) times larger than the activity of the \(P\) isomers. In these TRR spectra no band belonging to the \(P\) form was identified; hence the most intense among such bands can be assumed to be at least 20 times weaker than the strongest band of the \(E\) form. In view of the different scattering efficiency of the two isomers, the dominance of the \(E\) isomer in the TRR spectra is compatible with a population ratio \(N_E/N_P \gg 0.01\). With use of the Boltzmann relation and room temperature, this ratio suggests that the \(P\) form cannot be lower than by more than \(\sim 2.7\) kcal/mol (depending on the number of distinct species) than the \(E\) isomer.

A qualitative representation of the \(T_1\) PES of the \(1Xt\) conformer of DMHT, along the torsion around the central \(\text{C} = \text{C}\) bond, based on the above discussion, is shown in Figure 7. For comparison with unsubstituted 1,3,5-hexatriene, the reader is referred to Figure

\footnotetext{(22) Sandros, K.; Becker, H.-D. Photochem. 1987, 39, 301.}
forms, while the deactivation takes place at the perpendicular form. Similar to the one prevailing in naphthylethylene, the energy gap to the ground state. In this respect the situation is of 1,3,5-hexatriene shows nearly isoenergetic minima at planar E and Z geometries, the introduction of methyl groups in 2- and 5-positions causes considerable distortion of the T1 surface. In particular, the energy of planar (Z)-DMHT is raised by non-bonded interaction. Furthermore, steric interaction leads to a change in C–C single bond conformation in both the S0 and T1 when going from HT to DMHT. The influence of these changes on the quantum yields of E → Z and Z → E isomerization is yet to be investigated.

Figure 7. Qualitative potential energy surface of the cXt conformer of DMHT in the T1 and S0 states along the torsion of the central CC bond. See text for discussion.

10 of the previous paper in this issue. (It should be mentioned that the PES for the cXt conformer of DMHT differs somewhat from the picture given in Figure 7; this will be the subject of future work.) In both DMHT and HT the E and twisted minima are roughly at the same energy (within less than 1 kcal/mol) and are separated by a barrier sufficiently low to allow equilibration during the T1 lifetime. Both forms are substantially populated. The Z form is quasi-degenerate with the E form in HT, but is considerably higher, by 5–7 kcal/mol, in DMHT because of steric repulsion. Thus, at room temperature, the population of the Z form is negligible in DMHT, but substantial in HT.

Only the planar forms (only the E form in DMHT) contribute to the transient RR spectra. The twisted form does not contribute significantly, since the exciting wavelength is off-resonance with respect to the intense T1 → T0 transition. However, at the twisted form the T1 deactivation does take place, because of the small energy gap to the ground state. In this respect the situation is similar to the one prevailing in naphthylethylene, where the transient T1→T0 absorption from T1 is mostly due to the planar forms, while the deactivation takes place at the perpendicular form.

Conclusion

We have interpreted the T1 resonance Raman spectra of DMHT and of its deuterated isotopomers and we have assigned them to the E form of the conformers prevailing in each of the E and Z isomers in the equilibrated ground state.

The lack of observation of bands belonging to the Z form is explained in terms of nonbonded interactions, which lead to a higher energy than in the E form and hence to a smaller population in the thermally equilibrated triplet. The lack of contributions to the T1 TRR spectra from the P form is attributed in part to its smaller scattering efficiency, due to its preresonance character, in comparison with the in-resonance character of the scattering from the E isomer. An estimate of the ratio between the scattering activities of the two forms leads to a lower limit for the population ratio \( N_T / N_E \) of 0.01. This indicates that the relative minimum in the T1 potential energy curve found by some calculations at the twisted geometry is lower than the E energy by at most 2.7 kcal/mol.

A comparison with the previously discussed case of parent 1,3,5-hexatriene indicates that while the potential energy surface of 1,3,5-hexatriene shows nearly isoenergetic minima at planar E and Z geometries, the introduction of methyl groups in 2- and 5-positions causes considerable distortion of the T1 surface. In particular, the energy of planar (Z)-DMHT is raised by non-bonded interaction. Furthermore, steric interaction leads to a change in C–C single bond conformation in both the S0 and T1 when going from HT to DMHT. The influence of these changes on the quantum yields of E → Z and Z → E isomerization is yet to be investigated.

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Registry No. (E)-2,5-Dimethyl-1,3,5-hexatriene, 41233-74-3; (Z)-2,5-dimethyl-1,3,5-hexatriene, 49839-76-1; (E)-3,4-d2-2,5-dimethyl-1,3,5-hexatriene, 117566-51-5; (Z)-3,4-d2-2,5-dimethyl-1,3,5-hexatriene, 134879-35-9; (E)-3-d-2,5-dimethyl-1,3,5-hexatriene, 117566-50-4.

Supplementary Material Available: Computed wavenumbers, assignments, and Stokes shift parameters \( \gamma \) for the tZt, tZe, cZc, tPt, cPc, and tPc forms of DMHT and some of their deuterated derivatives (7 pages). Ordering information is given on any current masthead page.