Analysis of the rotational structure in the high-resolution infrared spectra of *trans*-hexatriene-2- d_1 and -3- d_1

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ABSTRACT

The 2- d_1 and 3- d_1 isotopologues of *trans*-hexatriene have been synthesized, and their high-resolution (0.0015 cm^{-1}) IR spectra have been recorded. For each of the isotopologues the rotational structure in four C-type bands for out-of-plane vibrational modes has been analyzed, and the ground state combination differences (GSCDs) have been pooled. Ground state rotational constants have been fitted to the GSCDs. For the 2-d species, A_0 , B_0 , and C_0 values of $0.7837254(5)$, $0.0442806(3)$, and $0.0419299(2)\text{ cm}^{-1}$ were fitted to 2450 GSCDs. For the 3-d species, A_0 , B_0 , and C_0 values of $0.7952226(8)$, $0.0446149(7)$, and $0.0422661(4)\text{ cm}^{-1}$ were fitted to 2234 GSCDs. For the eleven out-of-plane modes of the two isotopologues, predictions of wavenumbers corrected for anharmonicity and harmonic intensities have been computed and compared with experiment where possible.

Keywords

trans-hexatriene-2- d_1 and -3- d_1 , high-resolution infrared, vibration wavenumbers, rotational analysis, rotational constants, C-type bands

1. Introduction

The ultimate goal of this investigation is determining a semiexperimental equilibrium structure for *trans*-hexatriene (tHTE). The structure of this molecule is of significance as an instance of the effects of delocalized π -bonding. It is expected that blurring of the difference between the length of the localized sp^2 - sp^2 single bond and the lengths of localized C=C double bonds increases in comparison with 1,3-butadiene. The beginning of this blurring has been seen in butadiene [1], for which the comparative localized bond lengths were computed at a high level of theory for 90° twisted butadiene [2]. Pairs of p-orbitals are orthogonal when butadiene is twisted 90° around the single bond, and thus π -electron delocalization is quenched in this transition state. An equilibrium structure for *cis*-hexatriene (cHTE), derived from microwave (MW) spectroscopy, has already shown the anticipated structural effects [3,4] of greater π -electron delocalization as the polyene chain length increases. However, the two isomers of hexatriene are expected to display different structural consequences of π -electron delocalization.

To obtain a semiexperimental structure, rotational constants for a full set of isotopologues are sought. For nonpolar tHTE MW spectroscopy does not apply. Previously, high-resolution IR spectroscopy yielded rotational constants for *trans*-hexatriene [5], the 1,1- d_2 species [6], the *cis*-1- d_1 species [6], and the 1- $^{13}C_1$ species [7]. As part of the work on the 1- $^{13}C_1$ species, it was shown that the rotational constants for the 2- $^{13}C_1$ and 3- $^{13}C_1$ species could be predicted from quantum chemical (QC) calculations with good accuracy [7]. Remaining to be found are the ground state (GS) rotational constants for the 2- d_1 and 3- d_1 species. Their determination is the subject of the current investigation.

Samples of *trans*-hexatriene-2- d_1 and -3- d_1 (tHTE-2-d and tHTE-3-d) came from the same syntheses as were reported for deuterium isotopologues of cHTE [4]. Different synthetic routes were used for the two isotopologues.

2. Experimental

2.1. Syntheses

Syntheses of tHTE-2-*d* and tHTE-3-*d* were part of the work on cHTE [4]. Because the equilibrium between the two isomers of HTE substantially favors the trans isomer, this isomer was easy to isolate by preparative gas chromatography. Samples of less than 1 mmol were obtained. Carbon dioxide was removed from the samples by distillation through a column packed with Ascarite (Thomas Scientific), which is sodium hydroxide on a solid support. Water is added to a sample in this step. In a final step, the samples were dried by distillation through a column packed with phosphorus pentoxide and glass wool. Such samples, accompanied by a small amount of hydroquinone as a polymerization inhibitor, were flame sealed in borosilicate glass tubes for shipping. Sealed sample tubes were stored at -80°C except during shipping. Because no bands from the d_0 isotopic species were seen in the IR spectra of either d_1 isotopologue, isotopic purity was judged to be quite high.

During recording of high-resolution spectra over many hours, some air leaked into the White cell, which reintroduced CO₂ and H₂O lines into the spectra.

2.2. Spectroscopy

Medium-resolution IR spectra were recorded in the gas phase with a Nicolet 6700 FT spectrometer at a resolution of 0.1 cm⁻¹. 300 sample scans were made along with 300 scans of the empty cell, which had a 10 cm path length and KBr windows of 25 mm diameter. The IR spectrum of the 2-*d*₁ sample is in Figures S1a and S1b in the Supplementary Material. The IR spectrum of the 3-*d*₁ sample is in Figures S2a and S2b.

High-resolution IR spectra were obtained with a Bruker IFS 125HR spectrometer at PNNL. The beamsplitter was potassium bromide, the detector was a liquid-nitrogen-cooled HgCdTe device, and the resolution was 0.0015 cm⁻¹ for all spectra. Samples were contained in a White cell with a pathlength of 16 m. Spectra were post-recording zero-filled x8. Calibration was done with N₂O or OCS lines from the NIST on-line reference table [8], with CO₂ lines from the HiTran 2004 database [9], or with H₂O lines, as reported by Toth [10]. Conditions for recording different

spectra are in Table 1. Due to air leakage, in the worse case (Table 1), the pressure rose to 1.5 Torr in the White cell. This pressure broadening is approximately 0.00050 cm^{-1} [11], which is well inside the resolution used.

2.3. Computations

Vibration wavenumbers, anharmonic and harmonic, and harmonic IR intensities were computed with the B3LYP/cc-pVTZ model, using Gaussian03 (G03) software [12]. For these calculations the Cartesian coordinates were rotated into the principal axis system (PAS) of each isotopologue prior to use in the vibration-rotation module of G03 [13]. Fermi resonance adjustments were made for states of the same symmetry when they were within 100 cm^{-1} in the harmonic approximation.

A Loomis-Wood (LW) pattern recognition program was essential for displaying and finding series in the complex spectra [14]. A number of locally written Fortran programs were helpful in processing the large data sets and in developing large sets of quantum numbers for use in predicting transitions.

A modification of Arthur Maki's ASYMBD7 Fortran program was used to fit rotational transitions to Watson-type rotational Hamiltonians [15]. An asymmetric rotor reduction was used with the I_r representation. For the near-prolate top molecules ($\kappa \approx -0.99$) of interest in this work, using the alternative of a symmetric rotor reduction had a negligible effect on the fits of A_0 , B_0 , and C_0 . Data sets were not robust enough to fit the off-diagonal quartic centrifugal distortion constants, δ_J and δ_K . These constants were computed with the B3LYP/cc-pVTZ model in the vibration-rotation module of G03 and were used in fitting rotational constants. For determining GS rotational constants, fits were made to ground state combination differences (GSCDs), for which $\Delta J = 2$ and $\Delta K_a = 2$. When fitting transitions to rotational constants for an upper state (US), the GS rotational constants were held constant at values obtained in a GS fit.

3. Results

3.1. Selection rules for rotational transitions.

All of the bands analyzed for the two molecular species were C-type. For C-type transitions the selection rules for rotational transitions are $\Delta J = 0, \pm 1$; $\Delta K_a = \pm 1$; $\Delta K_c = 0$. Because only $^R R_K$ and $^P P_K$ series were found, ΔJ was limited to ± 1 . C-type bands have distinct, almost equally spaced Q branches for subbands, which can usually be indexed as a starting point for an analysis. In addition, the analysis of rotational structure in C-type bands gives a good definition of all three rotational constants, A_0 , B_0 , and C_0 . For the bands of tHTE in the low wavenumber region of this study, Doppler broadening is less than the resolution of 0.0015 cm^{-1} .

3.2. Predictions and assignments for vibrational transitions.

The structures of tHTE-2-d and tHTE-3-d are shown schematically in Figure 1, where the a axis for the smallest principal moment of inertia lies in the plane of symmetry and passes close to the C1 and C6 atoms. The b axis for the intermediate principal moment of inertia is perpendicular to the a axis in the plane of symmetry. The c axis for the largest principal moment of inertia is perpendicular to the molecular plane. The molecules are near-prolate symmetric tops.

Both molecules have low C_s symmetry. As a consequence, each molecule has 25 in-plane vibrational modes of the a' symmetry species and 11 out-of-plane modes of the a'' symmetry species. The a' modes have hybrid A/B band shapes in gas-phase IR spectra, and the a'' modes have C-type band shapes. C-type bands have prominent central Q branches. Supplementary Figures S1a,b and S2a,b give the gas-phase IR spectra of the 2-d and 3-d species, respectively, at moderate resolution.

Table 2 provides predictions and observations for vibrational modes of a'' symmetry. The table is limited to the out-of-plane modes because only C-type bands are analyzed in this report. Predictions of anharmonic frequencies were made with the B3LYP/cc-pVTZ model and the vibration-rotation module of G03. The predictions of intensities were at the harmonic level. For the parent molecule, tHTE,

the out-of plane modes break into two symmetry species, a_u and b_g , where the five b_g modes are only Raman active. For the most part, the b_g modes of the parent correlate with the a'' modes of the tHTE-2-d and -3-d species that have very weak IR intensities. With two exceptions, observed frequencies lie less than 20 cm^{-1} below the predicted frequencies. In Table 2, observed frequencies are given to decimal significance when the rotational structure in the band has been analyzed. Observed intensities are in qualitative agreement with the predictions. Except for ν_{33} of both species the unobserved bands lie in the shadows of strong bands.

The rotational structure in four C-type bands has been analyzed for each of the two isotopic species. The corresponding vibrational modes for tHTE-2-d are ν_{26} , ν_{27} , ν_{29} , and ν_{32} . For the tHTE-3-d species, the vibrational modes are ν_{26} , ν_{28} , ν_{29} , and ν_{32} . Rotational analysis of several bands with common GSCDs confirms correct assignments.

3.3. Rotational analysis of C-type bands of trans-hexatriene-2-d₁.

3.3.1. ν_{29} . The first C-type band of the tHTE-2-d species to be analyzed was for ν_{29} at 901.4 cm^{-1} , which is shown in Figure 2. This band of strong intensity with a fairly narrow central Q branch promised reduced confusion from hot bands. In addition, subband Q branch features on the R and P sides were readily seen. Combs for PQ_K and RQ_K features are shown for $K_a' = 3$ to 19. Q branches for $K_a' = 15$ are missing because of intensities for these subbands being depressed by a strong perturbation. Unassigned Q branches reflect one or more hot bands. As is true of the other bands investigated here, this band for ν_{29} is not baseline resolved due to the high density of weak lines. The ν_{29} vibrational transition is principally out-of-plane flapping of the two CH_2 groups in the same direction with a larger contribution from the cis (to C-C) C_6H bond in the half of the molecule away from the side of deuterium substitution.

Figure 3 is an enlargement of a limited portion of the R branch of the ν_{29} band from 909 to 912.5 cm^{-1} . Prominent subband Q branches, RQ_5 , RQ_6 , and RQ_7 , are

seen along with a number of unlabeled Q branches from hot bands. Assigned sequences for ${}^R R_4$ and ${}^R R_5$ are shown. Resolvable asymmetry splitting, where K_c values differ by one unit, appears at the higher J values in the ${}^R R_4$ series. A few lines in the sequences are missing due to confusion by stronger features. As the figure shows, the signal/noise (S/N) for making assignments in this band is marginal. Without the power of the LW pattern recognition program, finding series in the dense spectrum would not have been feasible. An example of a Loomis-Wood display for the other isotopic species, tHTE-3-d, is in supplementary Figure S3. Sixteen subband series were assigned in the R branch, and sixteen subband series were assigned in the P branch for a total of 2114 lines. Asymmetry splitting was observed for ${}^R R_2$, ${}^R R_3$, ${}^R R_4$, ${}^R R_5$, ${}^P P_4$, ${}^P P_5$, and ${}^P P_6$, thereby reinforcing the determination of the splitting between B_0 and C_0 .

From the data set for the ν_{29} band, 826 GSCDs were obtained and used to initiate fitting GS rotational constants for tHTE-2-d. Table 3 gives the rotational constants fitted to the pooled set of GSCDs derived from all four bands that were analyzed. Supplementary Table S1 contains the GSCDs derived from the lines assigned from the band for ν_{29} . This table also contains the GSCDs derived from the analyses of the other bands of tHTE-2-d and gives the details of fitting the GS rotational constants.

Perturbations in the US of the ν_{29} band limited fitting lines to series with $K_a' = 3 - 8$. Thus, the fitted upper state rotational constants and the overall band center at 901.4 cm^{-1} are approximate. The uncertainty of 0.001 cm^{-1} in the fit of ν_0 for ν_{29} in Table 1 is misleadingly small here and elsewhere in the paper because of the limited data set used for the US fit. Supplementary Table S2 gives the lines used and the details for the upper state fit for ν_{29} with an addendum of all the other lines assigned for this band that were used to derive GSCDs but were not included in the US fit. Lines that were suppressed (zero weight when the obs – calc was $\geq 0.001 \text{ cm}^{-1}$) are included in Table S2 because many of these lines were used to derive GSCDs. In the fit of GSCDs, transitions with deviations $\geq 0.001 \text{ cm}^{-1}$ were omitted from the data set. These two practices were sustained throughout this work.

3.3.2. ν_{32} . The second C-type band to be analyzed for tHTE-2-d was for ν_{32} at 682.6 cm^{-1} . This mode involves a_u twisting of the two CH_2 groups with greater contributions from the trans (to C–C) CH bonds. Figure 4 is an overall scan of the ν_{32} band. This band seems overrun with lines from carbon dioxide and to a lesser extent from water. Carbon dioxide lines are designated with “c,” and water lines are designated with “w” [16]. The strong central Q branch of the CO_2 bending mode is at 667 cm^{-1} . Combs show assignments of the Q-branch features in the P and R branches of the band for ν_{32} . K_a' extends from 4 to 25 for the subbands. The broad central Q branch indicates the presence of several hot bands.

Figure 5 is a small portion of the P branch from 661 to 664.5 cm^{-1} . This segment includes the $^{\text{P}}\text{Q}_{13}$, $^{\text{P}}\text{Q}_{14}$, and $^{\text{P}}\text{Q}_{15}$ features, as well as unlabeled Q branches from hot bands. As this detail shows, the sharp, known lines for CO_2 and H_2O cause a negligible problem in making the assignments. Subband series for $^{\text{P}}\text{P}_{13}$ and $^{\text{P}}\text{P}_{14}$ are shown. As with the ν_{29} band, the S/N is marginal for finding subband series.

For the ν_{32} band, a total of 22 subbands were assigned in the P branch, and 22 subbands were assigned in the R branch. Having GSCDs from the ν_{29} band helped in launching the assignment for the ν_{32} band. From an initial assignment of a subband in one branch, the partner subband could be predicted with GSCDs. Finding a good series for the partner subband gave strong support to the developing assignment. A total of 3085 lines were assigned for the ν_{32} band. From these lines 1239 GSCDs were determined. These GSCDs were joined with those from the ν_{29} band in making an improved fit of GS rotational constants. Supplementary Table S1 contains these GSCDs as part of the fit made for GS rotational constants. Perturbations in the ν_{32} band prevented fitting lines to upper state rotational constants. The estimate of the band center at 682.61 cm^{-1} came from a polynomial fit to the Q branches of subbands. The assigned lines for this band are in supplementary Table S3.

3.3.3. ν_{27} . A partial analysis was made of the C-type band of moderate intensity for the ν_{27} mode of tHTE-2-d₁ at 949.1 cm⁻¹. This mode is principally out-of-plane flapping of the two innermost CH bonds (C3H and C4H) and opposite-sense out-of-plane bending of the C5H bond. This weaker band, which is shown in Figure 6, is severely overlapped in its P branch by the R branch of the much stronger band at 901.4 cm⁻¹. This overlapping limited the range of possible assignments in the P branch of the ν_{27} band even though a good Q-branch progression was evident in the R branch. Without the partner ${}^{\text{P}}\text{P}_{K+2}$ series to check an ${}^{\text{R}}\text{R}_K$ series with the aid of GSCDs, assignments of additional ${}^{\text{R}}\text{R}_K$ series were in doubt and also useless in contributing GSCDs. Combs for $K_a' = 5 - 8$ for the four assigned subbands in each branch are shown in Figure 6.

The analysis of the band for the ν_{27} mode yielded 378 lines and 147 GSCDs. Supplementary Table S4 gives the partial set of lines for $K_a' = 5 - 7$ that were used for a rough fit of US rotational constants. All of the values of centrifugal distortion constants were held at the GS values. The additional lines that were also used to derive GSCDs are in an addendum to this table. All the GSCDs from the analysis of ν_{27} are in supplementary Table S1, where they contribute to the full set of GSCDs used to fit the GS rotational constants.

3.3.4. ν_{26} . The fourth band of tHTE-2-d to be investigated was the C-type band for ν_{26} at 1002.7 cm⁻¹. This complex mode is largely C5H out-of-plane bending with lesser amounts of C3H and C4H out-of-plane bending in the same sense and C6H₂ twisting on the end away from deuterium substitution. As shown in Figure 7, this band has a broad central Q branch, reflecting much hot band activity. The comparable bands in the spectra of tHTE [5] and tHTE-1-¹³C₁ [7] near 1010 cm⁻¹ were hard to analyze. The band in the spectrum of tHTE-2-d was more difficult. We settled for a partial analysis. Combs are shown in Figure 7 for $K_a' = 4 - 8$.

A total of 238 GSCDs were derived from the assignments. These GSCDs are in supplementary Table S1 along with the GSCDs from the other three bands. GSCDs from the four bands were used collectively to fit the GS rotational constants. Details

of fitting the full set of 2450 GSCDs to GS rotational constants are in supplementary Table S1. For the fit, the two off-diagonal quartic centrifugal distortion constants, δ_J and δ_K , were held at predicted values. The GS rotational constants for tHTE-2-d are in the first data column in Table 3.

A rough fit of US rotational constants for the ν_{26} band was made to give an estimate of the band center at 1002.7 cm^{-1} . Table S5 contains the details of the fit, the lines fit, and an addendum of other lines assigned in this band. All of the centrifugal distortion constants were held at values transferred from the GS. The results of that fit of 291 lines from the series for $K_a' = 4-6$ are in Table 1. A total of 533 lines were assigned for this band. The value for the band center of ν_{26} given in Table 4 is over-determined statistically. Table 1 gives a better estimate to 0.1 cm^{-1} .

3.4. Rotational analysis of C-type bands of trans-hexatriene-3-d₁.

3.4.1 ν_{26} . In the spectrum of tHTE-3-d the C-type band for ν_{26} at 997.4 cm^{-1} was easier to analyze than its counterpart in the spectrum of the 2-d species. The normal mode for ν_{26} is complex. The largest contributions are from out-of-plane flapping for C2H and C5H above the same side of the molecule plane; C4H flapping and twisting of the two CH₂ groups also contribute. Figure 8 shows the overall structure of the band with combs for Q branches of subbands from $K_a' = 4-18$. Uneven spacing of the Q branches for $K_a' = 11$ reveals a strong perturbation in this state. LW pattern recognition was essential for making these assignments as for other assignments reported in this paper. Supplementary Figure S3 shows an example of an LW display [14] for subbands $^{\text{R}}\text{R}_6$ to $^{\text{R}}\text{R}_{13}$. From all the lines found in the R and P branches, 855 GSCDs were obtained. These GSCDs are in supplementary Table S6 along with the GSCDs derived from the analysis of the other three bands of tHTE-3-d. This table also gives the details of fitting the GS rotational constants, which are summarized in the first data column of Table 4.

To avoid a perturbation, a fit to US rotational constants for ν_{26} was made with lines in the subbands with $K_a' = 4-6$. The resulting US rotational constants and

the estimate of the band center are in the second data column in Table 4. The statistical estimate of the uncertainty for ν_0 of this band is far too small. A realistic estimate to 0.1 cm^{-1} is in Table 1. Supplementary Table S7 gives the lines used and the details of the fit of the US rotational constants. Additional lines assigned for the ν_{26} band are an addendum to Table S7. A total of 1938 lines were assigned.

3.4.2. ν_{28} and ν_{29} . Figure 9 shows the structure of the complex of three C-type bands in the spectrum near 905 cm^{-1} . The weaker central Q branch at 895 cm^{-1} is for ν_{30} , which is principally C4H out-of-plane bending and flapping of the C6H₂ bonds in the *opposite* sense on the end away from deuterium substitution. This band was too weak to analyze. The Q branch at 902.2 cm^{-1} is the center of the stronger band for ν_{29} . This mode is largely out-of-plane C1H₂ flapping on the half of the molecule containing the CD bond. The third Q branch at 908.8 cm^{-1} , which is the strongest band, is the center of the ν_{28} band. This mode is principally C4H out-of-plane bending accompanied by C6H₂ flapping in the *same* sense in the half of the molecule away from deuterium substitution. Unfortunately, the two strong bands are only 6.6 cm^{-1} apart in the spectrum, whereas the anharmonic prediction is a more favorable separation of 12 cm^{-1} . The observed separation is surprisingly small for two modes of the same symmetry. The predicted intensities have the band for ν_{29} 30% more intense than the band for ν_{28} ; the opposite intensity relationship is observed. Weaknesses in the predictions of frequencies and intensities for ν_{28} and ν_{29} must reflect deficiencies in the predicted potential energy surface for these close-lying modes.

Despite the proximity of the two bands, extensive assignments were made for both bands. Figure 9 displays combs for the Q branches of the subband series analyzed in the two bands. Longer runs of Q-branch series were found for the more intense band for ν_{28} at 908.8 cm^{-1} . These Q branches extend from $K_a' = 5 - 21$ to give 17 subbands for each branch. For the somewhat weaker band at 902.2 cm^{-1} , the assignments were limited to $K_a' = 7 - 14$ with gaps for $K_a' = 8$ and 10.

For the stronger ν_{28} band, 2042 lines were assigned. These gave 800 GSCDs, which are reported in supplementary Table S6. Perturbations toward the band center and beyond $K_a' = 8$ limited the fitting of US constants to the subband series with $K_a' = 6-8$. This fit gave an estimate of 908.84 cm^{-1} for the band center when the excessive precision in the fit of ν_0 is discounted, as well as US rotational constants; see Table 4. A better estimate was 908.80 cm^{-1} , as derived from a polynomial fit to all the Q branches of the subbands. The lines and the details of the US fit are in supplementary Table S8. Assigned lines used for GSCDs but not in the fit for US rotational constants are an addendum in Table S8.

For the weaker ν_{29} band, 713 lines were assigned. A rough fit of US rotational constants was made for the lines in the series with $K_a' = 7, 9, 11$. The rotational constants from this fit are in data column 4 in Table 4. For the band center, the value of 902.2 cm^{-1} is an estimate. Details of the fit for the US rotational constants are in supplementary Table S9. Other assigned subband series used to compute GSCDs are an addendum to this table.

3.4.3 ν_{32} . Analysis of the rotational structure in the C-type band for ν_{32} was difficult and incomplete. The band is shown in Figure 10, where the complication of many lines from carbon dioxide (“c”) and water (“w”) due to air leakage is obvious [16]. These impurity lines are stronger than in the comparable band for the 2-d species. In addition, as the location of ν_0 indicates, the stronger, likely feature for a central Q branch was not the correct choice. For the scan in Figure 10, the pressure was increased (0.50 Torr) thereby giving a dense band that is far from baseline resolved. S/N for this band was decidedly inferior to the S/N for the corresponding ν_{32} band of the 2-d species. The fragmentary designations of Q branches in the combs in the two sides of the band reveal that several tentative assignments for series were rejected. Without a heavy dependence on a bootstrap procedure based on predictions made with the aid of GSCDs fit to the other bands, it would have been impossible to find any series and the band center in this very dense band. Accepted subband series are for $K_a' = 8-11, 13, 17, 18$. The ν_{32} vibration is similar to the

corresponding mode (ν_{32}) of the 2-d species. The principal contributions are unbalanced a_u torsions of the two CH_2 groups with the trans (to C–C) CH bonds moving more.

For the ν_{32} band, 277 GSCDs contributed to the pool for fitting the GS rotational constants. To avoid perturbations, US rotational constants were fitted to lines in the subband series for $K_a' = 8\text{--}10$. The value of 678.6 cm^{-1} from this fit for the band center must be regarded as approximate, even though it was supported by 678.60 cm^{-1} from a polynomial fit to all the Q branches of the assigned subbands. Lines used and details of the US fitting are in supplementary Table S10. Other assigned lines used for GSCDs are an addendum to this table. A total of 612 lines were assigned for the ν_{32} band. The US rotational constants are in Table 4. These US constants are approximate because of the small data set far from the band center and because all the centrifugal distortion constants were held at the GS values.

The feature at 681 cm^{-1} could be the P branch of the overtone of $\nu_{24}(a')$ predicted at 703 cm^{-1} , but likely lower by $10\text{--}20\text{ cm}^{-1}$. A feature for a weaker R branch is also present. Another possibility is a combination band for $\nu_{23}(a') + \nu_{34}(a'') = 689\text{ cm}^{-1}$ (A''), which could be strengthened by FR with the fundamental. However, a more realistic prediction for this combination would be $10\text{--}20\text{ cm}^{-1}$ lower.

4. Conclusions

Samples of the 2-d and 3-d isotopologues of tHTE were synthesized in high isotopic purity.

Predictions of wavenumbers with anharmonic corrections and harmonic intensities for the a'' out-of-plane vibrational modes were made for tHTE-2-d and tHTE-3-d. Predicted wavenumbers were higher than the observed values and were mostly well within 21 cm^{-1} of observations. Predicted intensities were in qualitative agreement with the observations.

The rotational structure in four C-type bands in high-resolution IR spectra has been analyzed for tHTE-2-d and for tHTE-3-d. For the 2-d species the bands were for the out-of-plane vibrational modes, ν_{26} , ν_{27} , ν_{29} , and ν_{32} . For the 3-d species

the bands were for the out-of-plane modes, ν_{26} , ν_{28} , ν_{29} , and ν_{32} . For each isotopologue the GSCDs from all of the bands were pooled for use in fitting GS rotational constants, 2450 GSCDs for the 2-d species and 2234 for the 3-d species. The GS rotational constants were well determined with standard deviations in the range of 10^{-7} cm $^{-1}$.

A full set of GS rotational constants for isotopologues of *trans*-hexatriene is now available for use in determining a semiexperimental equilibrium structure of this substance. The results of the structure fitting will be the subject of another publication.

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Appendix A. Supplementary material

Supplementary materials associated with this article are available on Science Direct (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (<http://library.osu.edu/sites/msa/mas+hp.htm>). Supplementary data associated with this article can be found, in the online version, at http://_____.

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Table 1. Conditions for high-resolution IR spectra

	Range/ cm ⁻¹	Aperture/ mm	Pressure/ Torr	Temp/ °C	Number scans	Calibr. gas
tHTE-2-d	600-1000	1.3	0.18 ^a	24	4096	OCS
	800-1400	1.15	0.18 ^a	24	4096	N ₂ O
tHTE-3-d	600-1000	1.3	0.10 ^b	22	4608	CO ₂
	800-1400	1.15	0.10 ^b	22	4096	H ₂ O
	600-1000	1.3	0.50 ^c	22	4160	CO ₂

^a Pressure rose of 0.36 Torr due to air leaking in.

^b Pressure rose of 1.1 Torr due to air leaking in.

^c Pressure rose of 1.5 Torr due to air leaking in.

Table 2. Wavenumbers for out-of-plane fundamentals of *trans*-hexatriene-2-*d*₁ and -3-*d*₁ (in cm⁻¹).

	<i>trans</i> -hexatriene-2- <i>d</i> ₁				<i>trans</i> -hexatriene-3- <i>d</i> ₁			
	Pred		Obs		Pred		Obs	
	Freq. ^a / cm ⁻¹	<i>I</i> ^b /km mol ⁻¹	Freq./ cm ⁻¹	<i>I</i> ^c	Freq. ^a / cm ⁻¹	<i>I</i> ^b /km mol ⁻¹	Freq./ cm ⁻¹	<i>I</i> ^c
ν_{26}	1020	46	1002.7	ms	1015	44	997.4	ms
ν_{27}	963	20	949.1	m	1002	0.27		
ν_{28}	922	0.52			930	33	908.8	s
ν_{29}	917	67	901.4	s	918	43	902.2	sm
ν_{30}	894	0.18			909	16	895	m
ν_{31}	832 ^d	5.1	822	wm	790	1.6	770	w
ν_{32}	696 ^d	14	682.6	m	694 ^d	14	678.6	m
ν_{33}	595 ^d	0.16			575 ^d	0.88		
ν_{34}	236	1.5			248	1.4		
ν_{35}	218	0.099			210	0.0008		
ν_{36}	96	0.37			96	0.39		

^a Anharmonic wavenumbers from the B3LYP/cc-pVTZ model.

^b Intensity.

^c Qualitative intensities: s = strong, m = medium, w = weak.

^d Fermi resonance shift less than 2.5 cm⁻¹.

Table 3. Rotational constants for *trans*-hexatriene-2-*d*₁ (in cm⁻¹).

	ground state	ν_{26}	ν_{27}	ν_{29}
<i>A</i>	0.7837254(5)	0.782718(9)	0.77836(1)	0.778789(3)
<i>B</i>	0.0442806(3)	0.043105(2)	0.044293(6)	0.0442664(4)
<i>C</i>	0.0419299(2)	0.041929(3)	0.041933(6)	0.0419372(4)
$\delta_J \times 10^9$	0.11078 ^a	0.11078 ^a	0.11078 ^a	0.11078 ^a
$\delta_K \times 10^7$	0.10649 ^a	0.10649 ^a	0.10649 ^a	0.10649 ^a
$\Delta_K \times 10^5$	0.19207(7)	0.19207 ^b	0.19207 ^b	0.323(5)
$\Delta_{JK} \times 10^7$	-0.235(2)	-0.235 ^b	-0.235 ^b	-0.902(8)
$\Delta_J \times 10^8$	0.169(2)	0.169 ^b	0.169 ^b	0.1687(7)
κ	-0.99366	-0.9636	-0.9636	-0.9937
ν_0		1002.7	949.1	901.406(1)
s. d.	0.00035	0.0011	0.0021	0.00036
Δ^c	-0.1663	0.0682	-0.2384	-0.4954
No. lines	2450 ^d	291	265	798
K_a'	3–25	4–6	5–7	3–8
$J_{\max}$	93	78	73	86

^a Calculated with B3LYP/cc-pVTZ model. ^b Ground state value. ^c Inertial defect, $\Delta = I_c - I_a - I_b$. ^d GSCDs: 237 from the ν_{26} band; 148 from the ν_{27} band; 826 from the ν_{29} band; 1239 from the ν_{32} band.

Table 4. Rotational constants for *trans*-hexatriene-3-*d*₁ (in cm⁻¹).

	ground state	ν_{26}	ν_{28}	ν_{29}	ν_{32}
<i>A</i>	0.7952226(8)	0.792390(6)	0.791726(3)	0.796671(36)	0.79528(2)
<i>B</i>	0.0446149(7)	0.044619(3)	0.044571(1)	0.044675(4)	0.04449(6)
<i>C</i>	0.0422661(4)	0.042276(4)	0.042297(1)	0.042209(4)	0.04239(7)
$\delta_J \times 10^9$	0.1101 ^a	0.1101 ^a	0.1101 ^a	0.1101 ^a	0.1101 ^a
$\delta_K \times 10^8$	0.9110 ^a	0.9110 ^a	0.9110 ^a	0.9110 ^a	0.9110 ^a
$\Delta_K \times 10^5$	0.1773(2)	0.1773 ^b	0.1773 ^b	0.57(2)	0.1773 ^b
$\Delta_{JK} \times 10^7$	-0.276(3)	-0.38(7)	-0.276 ^b	-0.276 ^b	-0.276 ^b
$\Delta_J \times 10^8$	0.183(3)	0.182(4)	0.167(1)	0.207(3)	0.183 ^b
κ	-0.99376	-0.9938	-0.9939	-0.9935	-0.9944
ν_0		997.4114(2)	908.8427(1)	902.195(1)	678.627(1)
s. d.	0.00042	0.00037	0.00045	0.0023	0.0033
Δ^c	-0.2009	-0.3315	-0.9552	0.8796	-2.403
No. lines	2234 ^d	357	382	376	217
K_a'	4-21	4-6	6-8	7,9,11	8-10
$J_{\max}$	94	80	90	88	59

^a Calculated with B3LYP/cc-pVTZ model. ^b Ground state value. ^c Inertial defect, $\Delta = I_c - I_a - I_b$. ^d GSCDs: 855 from the ν_{26} band; 800 from the ν_{28} band; 302 from the ν_{29} band; 277 from the ν_{32} band.

Captions for Figures

Figure 1. Schematic structures of tHTE-2-d and tHTE-3-d with locations of the principal a and b rotation axes.

Figure 2. Structure of the C-type band for ν_{29} of tHTE-2-d.

Figure 3. Detail within the R branch of the band for ν_{29} of tHTE-2-d.

Figure 4. Structure of the C-type band for ν_{32} of tHTE-2-d. “c” for CO₂ and “w” for H₂O contaminant lines.

Figure 5. Detail within the P branch of the band for ν_{32} of tHTE-2-d.

Figure 6. Structure of the C-type band for ν_{27} of tHTE-2-d.

Figure 7. Structure of the C-type band for ν_{26} of tHTE-2-d.

Figure 8. Structure of the C-type band for ν_{26} of tHTE-3-d.

Figure 9. Overlapped C-type bands for ν_{30} , ν_{29} , and ν_{28} of tHTE-3-d.

Figure 10. Structure of the C-type band for ν_{32} of tHTE-3-d. “c” for CO₂ and “w” for H₂O contaminant lines.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

TOC Graphic