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) 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) 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.

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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 CO_2 and H_2O 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 Figs. S1a and b in the Supplementary Material. The IR spectrum of the 3-d_1 sample is in Figs. S2a and b.

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 ×8. Calibration was done with N_2O or OCS lines from the NIST on-line reference table [8], with CO_2 lines from the HiTran 2004 database [9], or with H_2O 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 ^RR_K and ^PP_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 Fig. 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 Figs. 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

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_2O
tHTE-3-d	600–1000	1.3	0.10[b]	22	4608	CO_2
	800–1400	1.15	0.10[b]	22	4096	H_2O
	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.