

Supporting Information

Microwave Spectra of the Deuterium Isotopologues of *cis*-Hexatriene and a Semiexperimental Equilibrium Structure

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Table S1. Ab initio structures for *cis*-Hexatriene (in Å and deg).

Table S2. Values of $\Delta I = I(\text{isotopologue}) - I(\text{parent})$ (uÅ^2)

Figure S1a. Gas phase infrared spectrum of a mixture of *cis*-hexatriene-1,1-d₁, -*cis*-1-d₁, and -*trans*-1-d₁. 4000-2000 cm^{-1} . 16 scans. Pressure 16 Torr. Resolution 0.5 cm^{-1} .

Figure S1b. Gas phase infrared spectrum of a mixture of *cis*-hexatriene-1,1-d₁, -*cis*-1-d₁, and -*trans*-1-d₁. 2000-400 cm^{-1} . 16 scans. Pressure 16 Torr. Resolution 0.5 cm^{-1} . tHTE- 1-d₁: 852 cm^{-1} .

Figure S2a. Gas phase infrared spectrum of *ca* 2 parts *cis*-hexatriene-2-d₁:1 part *trans*-hexatriene-2-d₁. 4000-2000 cm^{-1} . 16 scans. Pressure 18 Torr. Resolution 0.5 cm^{-1} .

Figure S2b. Gas phase infrared spectrum of *ca* 2 parts *cis*-hexatriene-2-d₁:1 part *trans*-hexatriene-2-d₁. 2000-400 cm^{-1} . 16 scans. Pressure 18 Torr. Resolution 0.5 cm^{-1} . tHTE: 1808, 1618, 1160, 1001, 901.4, 822, and 683 cm^{-1} . CH₂Cl₂ impurity: 1268 and 759 cm^{-1} .

Figure S3a. Gas phase infrared spectrum of *cis*-hexatriene-3-d₁. 4000-2000 cm^{-1} . 300 scans. Spectrometer purged with dry N₂. Pressure 20 Torr. Resolution 0.1 cm^{-1} .

Figure S3b. Gas phase infrared spectrum of *cis*-hexatriene-3-d₁. 2000-400 cm^{-1} . 300 scans. Spectrometer purged with dry N₂. Pressure 20 Torr. Resolution 0.1 cm^{-1} . CH₂Cl₂ impurity: 1268 and 759 cm^{-1} .

Table S1. Ab initio structures for *cis*-Hexatriene (in Å and deg).

Internal coord.	MP2 (AE)	MP2 (AE)	CCSD(T) (AE)	MP2(FC)	MP2(FC)
	cc-pwCVTZ	cc-pwCVQZ	cc-pwCVTZ	cc-pVQZ	aug-cc-pVQZ
$r(\text{C1C2})$	1.3380	1.3368	1.3413	1.3405	1.3412
$r(\text{C2C3})$	1.4446	1.4429	1.4543	1.4465	1.4467
$r(\text{C3C4})$	1.3484	1.3473	1.3501	1.3510	1.3516
$r(\text{C1H1 cis})$	1.0804	1.0796	1.0831	1.0812	1.0816
$r(\text{C1H1 trans})$	1.0782	1.0774	1.0807	1.0789	1.0793
$r(\text{C2H2})$	1.0809	1.0802	1.0830	1.0818	1.0822
$r(\text{C3H3})$	1.0831	1.0824	1.0847	1.0840	1.0844
$\alpha(\text{C1C2C3})$	122.788	122.734	122.843	122.717	122.698
$\alpha(\text{C2C3C4})$	126.216	126.175	126.293	126.157	126.100
$\alpha(\text{C2C1H1 cis})$	120.882	120.847	121.055	120.838	120.825
$\alpha(\text{C2C1H1 trans})$	121.450	121.428	121.523	121.412	121.410
$\alpha(\text{C1C2H2})$	118.692	118.680	118.900	118.692	118.696
$\alpha(\text{C4C3H3})$	117.877	117.891	118.024	117.896	117.924

Table S2. Values of $\Delta I = I(\text{isotopologue}) - I(\text{parent})$ ($\text{u}\text{\AA}^2$)

	A_e^a	B_e^a	C_e^a	AI ^a			SE ^b			$\delta\Delta I_b^c$
				ΔI_a	ΔI_b	ΔI_c	ΔI_a	ΔI_b	ΔI_c	
N	14798.58	1590.38	1436.05							
1-13C	14753.43	1550.51	1403.05	0.10	8.17	8.28	0.10	8.17	8.27	0.003
2-13C	14727.22	1578.79	1425.93	0.17	2.33	2.50	0.17	2.33	2.49	0.002
3-13C	14554.34	1588.12	1431.88	0.57	0.45	1.02	0.57	0.45	1.02	0.000
1,1-d2	14032.25	1482.48	1340.82	1.87	23.13	24.99	1.86	23.12	24.98	0.011
trans 1-d1	14213.70	1531.74	1382.73	1.41	12.16	13.57	1.40	12.16	13.56	0.001
cis 1-d1	14636.00	1535.70	1389.87	0.38	11.31	11.69	0.38	11.31	11.69	0.007
2-d1	14016.19	1584.68	1423.71	1.91	1.14	3.05	1.91	1.12	3.03	0.022
3-d1	13633.51	1583.36	1418.61	2.92	1.41	4.33	2.91	1.41	4.32	-0.003

^a From the ab initio structure, column 5 of Table 6.

^b From the semiexperimental rotational constants, Table 4.

^c $\delta\Delta I_b = \Delta I_b(AI) - \Delta I_b(SE)$.

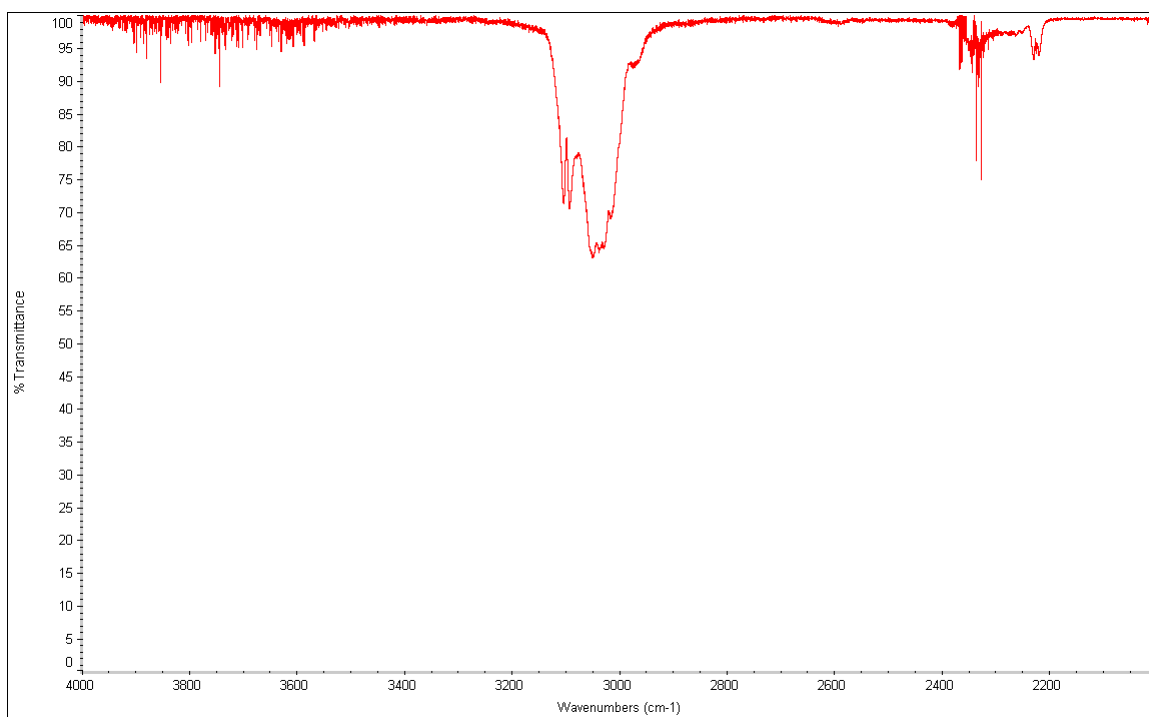


Figure 1a.

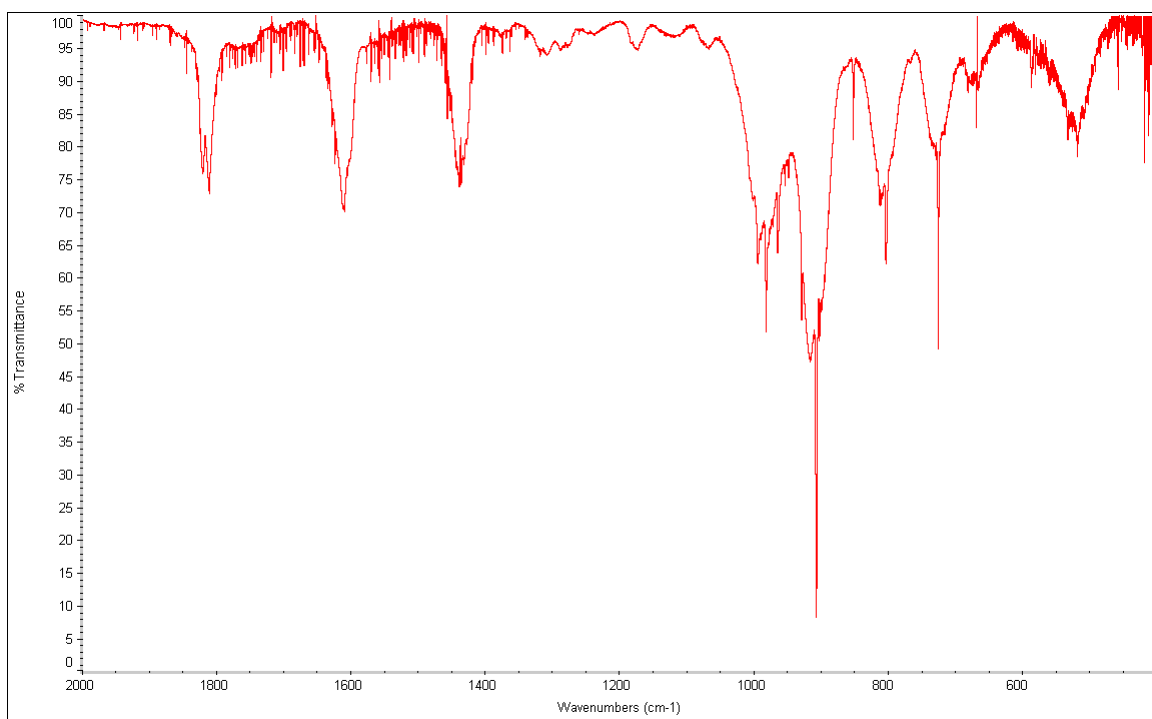


Figure 1b.

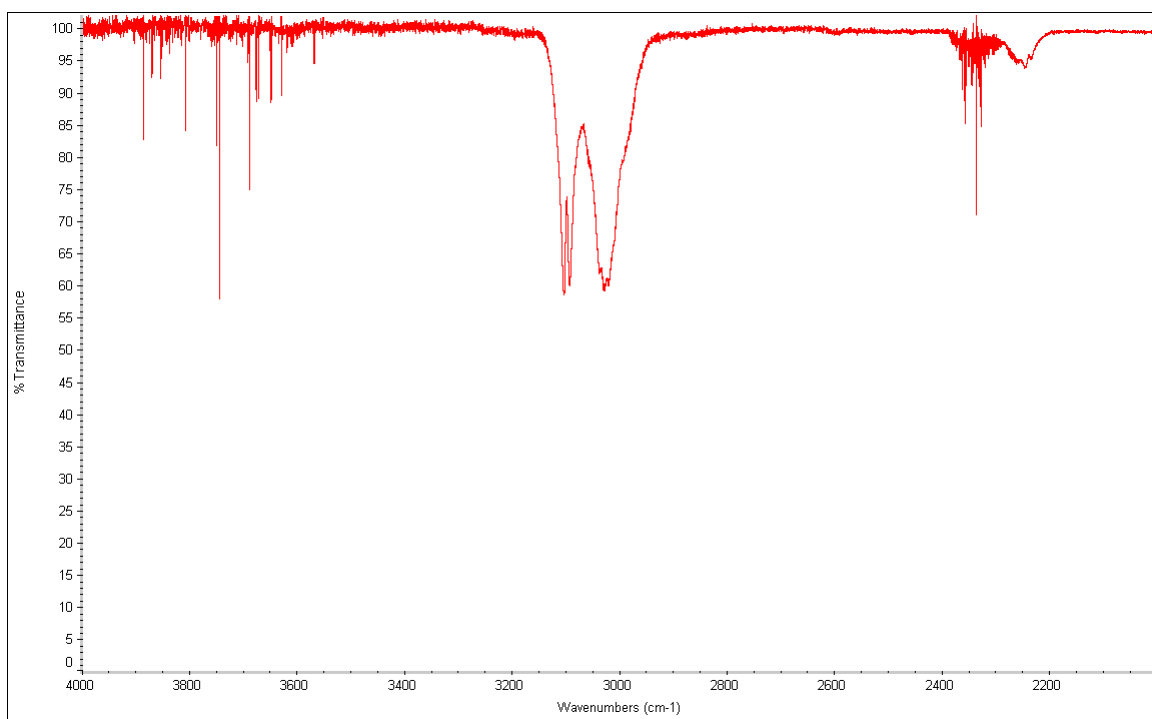


Figure 2a.

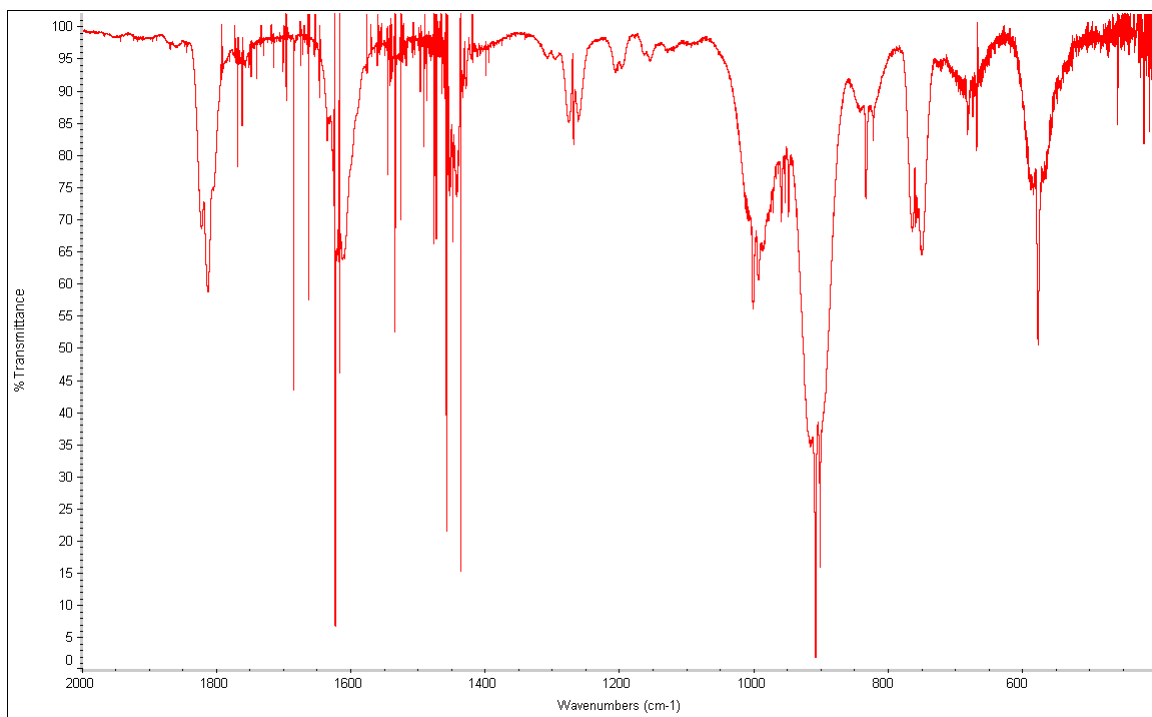


Figure 2b.

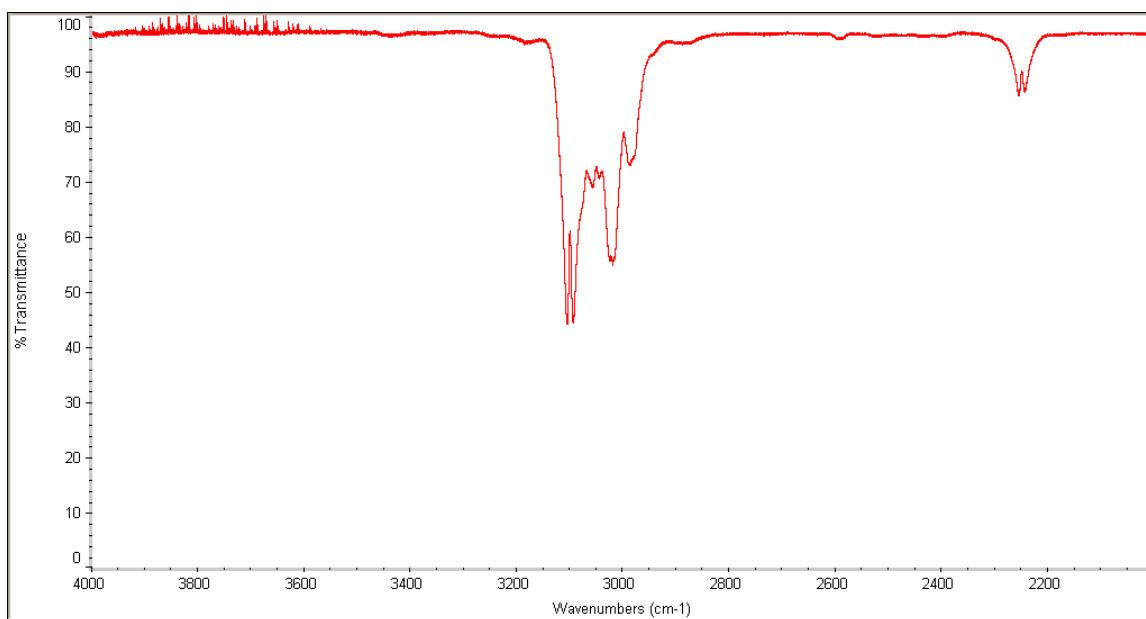


Figure 3a.

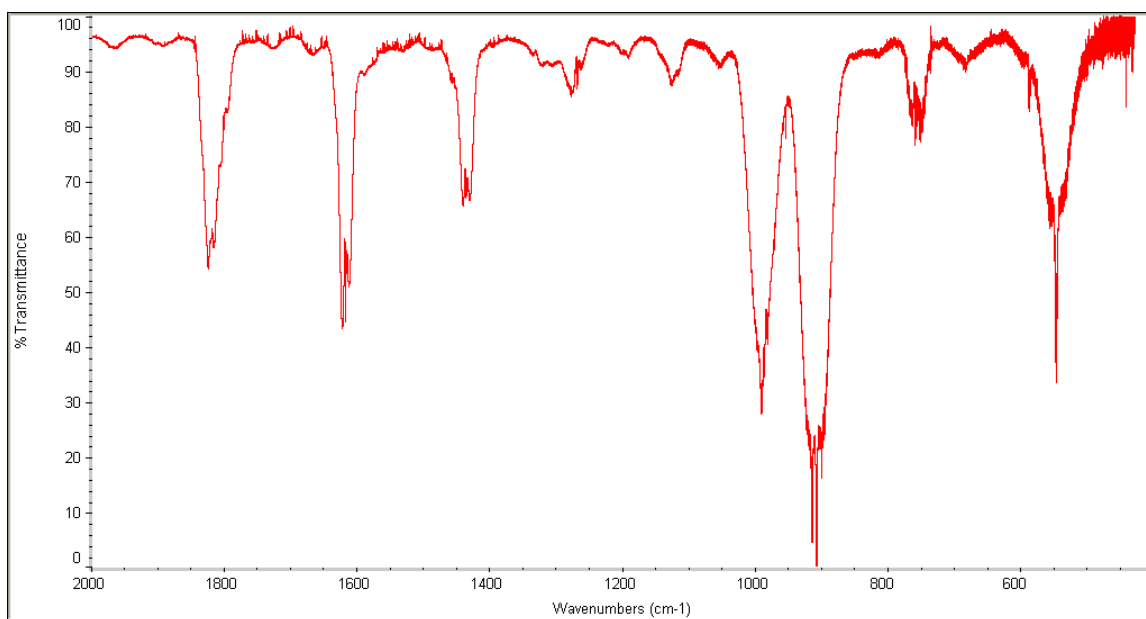


Figure 3b.