THE LAST LAP: HIGH-RESOLUTION INFRARED SPECTROSCOPY OF BUTADIENE-2.3-$^{13}C_2$.

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This report on the high-resolution (0.002 cm^{-1}) infrared spectroscopy of butadiene-2,3-$^{13}C_2$ is a culmination of the investigation of rotational constants of a series of isotopomers of butadiene (BDE). The goal is an equilibrium structure of butadiene with which to answer a question. Does the structure of butadiene reflect pi-electron delocalization? Ground state rotational constants are now available for BDE, BDE-2,3-d_2,[a] BDE-1,1-d_2,[b] BDE-trans,trans-1,4-d_2, BDE-cis,trans-1,4-d_2, BDE-cis,cis-1,4-d_2,[c] and BDE-1-$^{13}C_1$.[d] BDE-2,3-$^{13}C_2$ has been synthesized and its ground state rotational constants have been derived from the analysis of a C-type band arising from CH_2 flapping at 907.1722 (2) cm^{-1}. These values, which are fit to 1184 ground state combination differences, include A = 1.3545028 (6), B = 0.1469410 (2), and C = 0.1325846 (2) cm^{-1}. Medium-resolution infrared and Raman spectroscopy have led to a complete assignment of vibrational fundamentals, which are useful in assessing a new force field for butadiene. The new force field depends on selectively scaled force constants in symmetry coordinate space. The final step in this project is obtaining good vibration-rotation alphas predicted by quantum chemical calculations for use in extracting equilibrium rotational constants and an equilibrium structure.

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