ISOTOPOLOGUE AND ISOTOPOMER ANALYSIS OF DEUTERATED CYCLOHEXENE USING MOLECULAR ROTATIONAL RESONANCE SPECTROSCOPY

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Molecular rotational resonance (MRR) spectroscopy was used to identify and quantitate the relative abundance of cyclohexene isotopologues prepared from a tungsten-benzene complex. Of the 1024 possible deuterium isomers, 992 of the geometries are pairs of rotationally equivalent geometries producing only 496 isomers with distinguishable rotational spectra. In addition, there are 32 species that yield identical structure for C2-rotation. Therefore, there are 528 different deuterium isomers that have distinguishable rotational spectra. Due the transient chirality associated with the ring pucker of cyclohexene, each isotopomer typically has two rotationally distinct forms in the sample. A rotational spectroscopy methodology was developed to perform automated isotopologue and isotopomer analysis of the synthetic samples. The analysis uses a single reference geometry to identify the isomers. The reference structure is obtained from the singly-substituted ^{13}C, doubly-substituted ^{13}C, and singly-substituted deuterium isotopomer rotational constants that are obtained from measurements in natural abundance using a commercial cyclohexene sample. In total, 26 deuterium isomers were identified in various samples of isotopically enriched cyclohexene. Of these 26 isomers represent 15 chemically distinct species. The confidence of the identification is assessed by comparing the root-mean-squared (RMS) error for the three rotational constants of each species. In all cases, the experimental rotational constants can be attributed to a single isotopomer with high confidence. This analysis demonstrates the potential for routine, fast isotopomer identification that provides site-specific information of deuterium incorporation. For the cyclohexene samples prepared using the tungsten complex, rotational spectroscopy verified high stereoselectivity in the synthesis with about 1% or less over- and under-deuteration in most cases.