ANALYSIS OF THE ROTATIONAL STRUCTURE IN THE HIGH-RESOLUTION INFRARED SPECTRUM OF *TRANS*-HEXATRIENE-1-$^{13}C_1$

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Hexatriene-1-$^{13}C_1$ was synthesized by reaction of 2,4-pentadienal and (methyl-^{13}C)-triphenylphosphonium iodide (Wittig reagent). The *trans* isomer was isolated by preparative gas chromatography, and the high-resolution (0.0015 cm^{-1}) infrared spectrum was recorded on a Bruker IFS 125HR instrument. The rotational structure in two C-type bands was analyzed. For this species the bands at 1010.7 and 893.740 cm^{-1} yielded composite ground state rotational constants of A_0 = 0.872820(1), B_0 = 0.0435868(4), and C_0 = 0.0415314(2) cm^{-1}. The ground state rotational constants for the 1-^{13}C species were also predicted with Gaussian 03 software and the B3LYP/cc-pVTZ model. After scaling by the ratio of the observed and predicted ground state rotational constants for the normal species, the predicted ground state rotational constants for the 1-^{13}C species agreed within 0.005 % with the observed values. Similar good agreement between observed and calculated values (0.016 %) was found for the three ^{13}C species of the *cis* isomer.[a] We conclude that ground state rotational constants for single heavy atom substitution can be calculated with adequate accuracy for use in determining semi-experimental equilibrium structures of small molecules. It will be unnecessary to synthesize the other two ^{13}C species of *trans*-hexatriene.

[a] R. D. Suenram, B. H. Pate, A. Lesarri, J. L. Neill, S. Shipman, R. A. Holmes, M. C. Leyden, N. C. Craig J. Phys. Chem. A 113, 1864-1868 (2009).