

ANALYSIS OF ROTATIONAL STRUCTURE IN THE HIGH-RESOLUTION INFRARED SPECTRA OF THE *TRANS*-HEXATRIENE-1,1-*D*₂ AND -*CIS*-1-*D*₁ SPECIES

NORMAN C. CRAIG, HANNAH A. FUSON, and HENGFENG TIAN, *Department of Chemistry and Biochemistry, Oberlin College, Oberlin, OH 44074*; THOMAS A. BLAKE, *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352*.

Hexatriene-1,1-*d*₂ with some admixture of the *cis*-1-*d*₁ and *trans*-1-*d*₁ species was synthesized by reaction of 2,4-pentadienal and (methyl-*d*₃)-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 for the 1,1-*d*₂ species was analyzed. For this species the bands at 902.043 and 721.864 cm⁻¹ yielded composite ground state rotational constants of $A_0 = 0.801882(1)$, $B_0 = 0.041850(2)$, and $C_0 = 0.039804(1)$ cm⁻¹. For the *cis*-1-*d*₁ species the C-type band at 803.018 cm⁻¹ gave $A_0 = 0.809384(2)$, $B_0 = 0.043530(3)$, and $C_0 = 0.041321(2)$ cm⁻¹. By iodine-catalyzed isomerization, we have obtained some of the much less favored *cis* isomer and hope to obtain microwave spectra for its three deuterium-substituted species. The rotational constants reported here contribute to data needed for determining a semi-experimental structure for *trans*-hexatriene, which should show that the structural consequences of *pi*-electron delocalization increase with the chain length of polyenes.