Microwave Spectrum, Dipole Moment, and a Proposed Structure for 1-Cyanobicyclo[1.1.0]butane

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The microwave spectra of the normal and the 2-13C isotopic species of 1-cyanobicyclo[1.1.0]butane have been observed and assigned, leading to the following rotational constants: (normal), \(A = 8807.202 \pm 0.004\), \(B = 2924.334 \pm 0.002\), \(C = 2509.322 \pm 0.002\) and (isotope), \(A = 8608.85 \pm 0.85\), \(B = 2902.88 \pm 0.02\), and \(C = 2478.56 \pm 0.02\) MHz. Measurements of the second-order Stark effect led to \(\mu_I = 4.08 \pm 0.01\) D. Based on the available microwave data coupled with geometry-optimized \textit{ab initio} molecular orbital structures for cyanocyclopropane and 1-cyanobicyclo[1.1.0]butane, a molecular structure for the latter molecule is proposed. Analysis of the dipole moments of these molecules and of bicyclo[1.1.0]butane has led to the conclusion that the bicyclobutyl group is a better electron donor than is cyclopropyl. In addition, a simple frontier molecular orbital model is not sufficient for explaining all of the structural changes that occur on substituting cyano at the bridgehead of bicyclo[1.1.0]butane.

INTRODUCTION

In recent structural studies from our laboratories we have reported several investigations of the \(\pi\)-conjugative interactions of the cyclopropyl ring with various substituents. In the cases where the substituent was cyano [1], acetylene [1] or cyclopentadienyl [2], the structural results were in excellent agreement with a frontier orbital model [3] involving \(\pi\)-electron donation from the highest occupied molecular orbital (HOMO) of cyclopropyl to the lowest unoccupied molecular orbital (LUMO) of the substituent. In the case of isocyano, the structural and theoretical results [4] suggested a HOMO\(\leftrightarrow\)HOMO (four-electron) \(\pi\)-interaction produced by the isocyano group in addition to a HOMO\(\leftrightarrow\)LUMO interaction as in the other three cases.

As a part of these ongoing studies, we have completed initial structural and dipole moment investigations of 1-cyanobicyclo[1.1.0]butane. This species, with its fused cyclopropyl rings, provides an interesting extension into the realm of the simplest bicyclic species. The parent molecule has been the subject of numerous theoretical investigations [5,6] and its structure was elucidated some years ago [7]. Its molecular orbital system has been extensively investigated [5,6] and, based on analogies to cyclopropane, it was expected to undergo substantial \(\pi\)-conjugation with cyano, a good \(\pi\)-acceptor.

EXPERIMENTAL

The sample of 1-cyanobicyclo[1.1.0]butane used in this study was prepared by the method of Hall et al. [8] from a sample of 3-chloro-1-cyanocyclobutane kindly provided by Dr. Tada Fukunaga of the DuPont Co.

Microwave spectra were obtained in the R-band by conventional methods using a Hewlett-Packard 8460 Stark-modulated microwave spectrometer. Radiofrequency-microwave double-resonance measurements (RFMDR) were also made by conventional methods [9,10]. Sample pressures were typically in the range of 10–50 mTorr (1–7 Pa) with the cell at either room or
dry-ice temperature. Hyperfine structure from the interaction of the $^{14}$N nuclear electric quadrupole moment with the overall rotation was not resolved, but produced slightly broadened and asymmetric lines in a few cases. In general, the reported transition frequencies are expected to have an accuracy of at least $\pm 0.1$ MHz.

Dipole moment measurements were performed by measuring frequency shifts of various $J,M$ components as a function of the applied ground-to-base voltage. Stark cell calibration was performed by observing the OCS Stark effect and by employing the known dipole moment value of 0.71521 D [11].

Ab initio molecular orbital calculations were performed with Pople's GAUSSIAN 82 series of programs [12], which employed the 3–21G [13] and 6–31G* [14] basis sets. Electron correlation was incorporated at the level of second-order Møller-Plesset (MP2) perturbation theory [15]. Structures were fully optimized at the RHF/3–21G, RHF/6–31G*, and MP2/6–31G* levels subject only to molecular-symmetry constraints.

**RESULTS**

**Observed Spectrum and Assignments**

Spectral assignments were made for the normal and the 2-$^{13}$C isotopic species in their natural isotopic abundances. The spectra consisted of characteristic clusters of intense $a$-type, R-branch lines. Initial assignments were performed by observing RFMDR transitions for two pairs of lines ($J = 6\rightarrow 5$ and $J = 7\rightarrow 6$). Following these assignments the normal species R-branch spectrum was easily assigned, and in addition, a large number of relatively weak $a$-type, Q-branch lines were identified and measured. The observed spectrum is given in Table 1 and the resulting rotational and distortion constants, obtained by fitting a standard $P^4$ Hamiltonian [16], are given in Table 2. The quality of the spectral fit, evidenced by the “obs-calc” values of Table 1, is very good. For the 2-$^{13}$C species, having intensities only 2% of the normal species, it was not possible to assign the very weak Q-branch transitions, and consequently the spectral constants are not as well determined. Table 3 presents the observed transitions while Table 2 summarizes the rotational constants obtained by using the same $P^4$ Hamiltonian. Since the