VIBRATIONAL AVERAGING, INERTIAL DEFECT AND THE MOLECULAR STRUCTURE OF o-BENZYNE[a]

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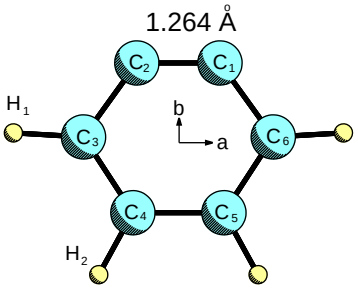

Rotational transitions for six isotopomers of o-benzyne were measured using a pulsed-beam, Fourier transform microwave spectrometer. The o-benzyne was efficiently produced with a dilute mixture of benzene in neon, flowing through a pulsed-DC discharge beam source. Although all reported transitions were measured to 1 to 2 kHz accuracy, and rotational constants were obtained with uncertainties less than 1 kHz, the first attempts to fit a planar structure to the measured rotational constants were not satisfactory. Vibrational averaging effects result in an inertial defect of Δ = 0.06935(1) amu Å^2. Although this small, positive value is consistent with a planar structure, the deviations from the least squares fit to calculate the atomic coordinates are as large as 1 MHz, if no vibrational averaging corrections are made. These deviations are approximately 1000 times experimental uncertainties. The key to improving the structural fits is to subtract calculated contributions to rotational constants, due to vibrational averaging from the measured rotational constants, and to include small, mass-dependent corrections to atomic coordinates. Even for this 10-atom molecule, calculating all of the vibrational averaging corrections from ab initio theory would be a formidable task. Fortunately Jim Watson provided a procedure to obtain approximate, harmonic vibrational corrections from the measured centrifugal distortion constants. This procedure allowed substantial improvements in the structural fitting. The resulting acetylenic C1-C2 bond length is 1.264(3) Å, and the other bond lengths are: C2-C3 = 1.390(3) Å, C3-C4 = 1.403(3) Å, C4-C5 = 1.404(3) Å, C3-H1 = 1.095(9) Å, and C4-H2 = 1.099(4) Å

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