The Microwave Spectrum and Planarity of Cyclopent-3-enone

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Summary. The ring atoms in cyclopent-3-enone are shown to be coplanar by a study of the rotational spectrum in the vibrational ground state and in several successive excited states of an out-of-plane ring vibration.

RECENT interest[1] in the nature of the potential functions governing the two puckering vibrations of five-membered rings has led to microwave-spectroscopic studies of several such molecules.[1-3] In particular, similar but unequal double minimum potential functions have been shown to be associated with the two puckering vibrations of cyclopentanone[3] so that the equilibrium ring atom configuration is nonplanar. This result is consistent with the expectation that planar cyclopentanone would have eclipsed methylenic hydrogen atoms and that therefore torsion would occur about the C–C bonds to produce the more favourable staggered situation in the nonplanar ring, even though this would involve a further decrease of already strained ring angles. For the closely related cyclopent-3-enone (see Figure 1), on the other hand, a planar ring is favoured both by the staggered ethylenic and methylenic hydrogen atoms and by ring angle strain. We report here the microwave spectrum of cyclopent-3-enone in the vibrational ground state and several successive excited states of the lowest out-of-plane ring vibration. We conclude that the potential function associated with the vibration has a single minimum and that the equilibrium configuration of the heavy atoms is planar.

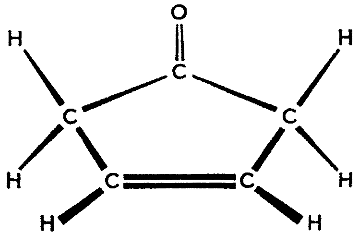

FIGURE 1

Cyclopent-3-enone is a near-prolate asymmetric rotor which exhibits *a*-type transitions only. Each of the low *J*, *R* branch transitions is accompanied to high frequency by a set of almost equally spaced vibrational satellites belonging to the first five excited states of an out-of-plane ring vibration. Ground-state transitions and vibrational satellites assigned with the help of Stark-effect patterns were used in rigid rotor, least-squares analyses to give the rotational constants and principal moments of inertia which are displayed in the Table for the states with $V = 0$ to $V = 5$. In order that non-rigid effects should be negligible only transitions with $J \leqslant 10$ were included in the least-squares analysis.

The planarity of cyclopent-3-enone is established by two arguments. The first of these involves the quantities $\Delta = I_c - I_b - I_a$ which are included for each vibrational state in the Table. For a planar heavy-atom skeleton, if zero-point vibrational effects are ignored, Δ is simply related to the out-of-plane co-ordinates (C_H) and masses (M_H) of the methylenic hydrogen atoms by $\Delta = -8M_HC_H^2$. Using the standard methylene group parameters $r_{C-H} = 1.09$ Å and ∠HCH = 109°28′, Δ is calculated as -6.386 a.m.u. Å^2, a value close enough to that observed for the vibrational ground state ($V=0$) to suggest strongly that the

TABLE

Rotational constants (MHz) and moments of inertia (a.m.u. Å^2)

	$V = 0$	$V = 1$	$V = 2$	$V = 3$	$V = 4$	$V = 5$
A	7378·18	7351·86	7326·28	7301·35	7276·56	7252·26
B	3615·168	3620·759	3626·157	3631·430	3636·642	3641·808
C	2503·581	2511·905	2519·808	2527·428	2534·839	2542·091
I_a	68·4960	68·7412	68·9813	69·2168	69·4526	69·6853
I_b	139·7932	139·5774	139·3696	139·1672	138·9678	138·7706
I_c	201·8613	201·1923	200·5613	199·9566	199·3720	198·8033
Δ	$-6·4279$	$-7·1263$	$-7·7896$	$-8·4274$	$-9·0484$	$-9·6526$

heavy atoms are coplanar, although a very small degree of nonplanarity cannot be ruled out. Furthermore, the progressively more negative value of Δ as the vibrational quantum number V increases is evidence that the vibrational motion takes the ring atoms out of the plane.

The second and more conclusive argument for planarity involves the variation of the rotational constants with the quantum number V. Figure 2 shows plots of the type $|g_V - g_0|$ against V, where g is one of the rotational constants A, B, and C. These smooth, almost linear, curves are to be expected if a nearly harmonic single minimum potential function governs the vibrational motion.[4] If the equilibrium structure of the ring were even very slightly nonplanar, corresponding to a double minimum potential function with a very low barrier at the planar configuration, the curves in Figure 2 would show a significant zig-zag effect between $V = 0$, 1, and 2 due to the differential perturbation of these states by the barrier, as observed for trimethylene oxide[4] and cyclobutanone.[5]

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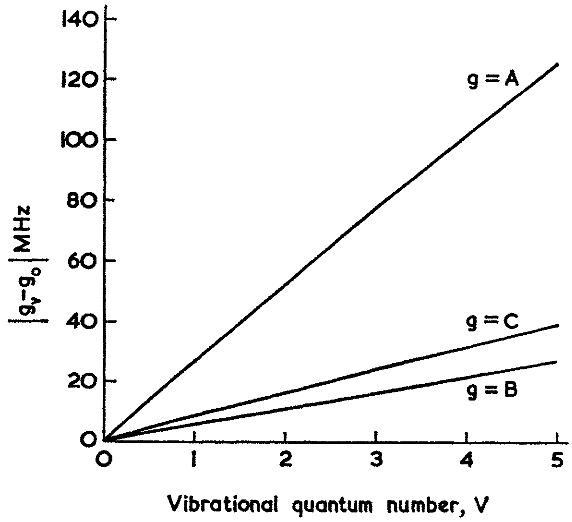

FIGURE 2

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