The Microwave Spectrum and Ring Planarity of Cyclopent-2-en-1-one

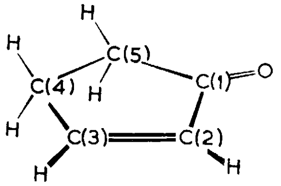
By D. CHADWICK, A. C. LEGON,* and D. J. MILLEN

(*William Ramsay and Ralph Forster Laboratories, University College, London, W.C.*1)

Summary The principal moments of inertia of two isotopic species of cyclopent-2-en-1-one, derived from their microwave spectra, show that the oxygen atom and the five carbon atoms are coplanar.

CYCLOPENT-2-EN-1-ONE (see Figure) is a ring system for which the configuration is decided by competition between several factors. The conjugated olefinic double bond and carbonyl group give the whole ring a preference for planarity. However, the coplanarity of all ring atoms results in an eclipsed configuration for the methylenic hydrogen atoms at C(4) and C(5). The staggered configuration is energetically more favourable than the eclipsed one but the torsion about the C(4)–C(5) bond required to achieve it would further decrease the already strained ring angles and would destroy the ring planarity. We have now studied the microwave spectra of the normal species and the [^{18}O]-substituted species of cyclopent-2-en-1-one and interpret the spectra in favour of a planar structure for the heavy atoms.

The microwave spectrum of cyclopent-2-en-1-one consists of many quite strong *a*-type transitions. Measurements were made in the frequency range 15—36 GHz and low J transitions assigned by Stark effect patterns and by double resonance techniques. A least-squares analysis of low J transitions showed them to fit rigid rotor theory very closely with negligibly small centrifugal distortion effects for $J < 10$. This molecule is free then from the kind of vibration–rotation interaction effects which cause large deviations from rigid rotor patterns in cyclopentene.[1] No inverson doubling was apparent in the spectrum and no transitions associated with any out-of-plane (c) component of dipole moment were revealed by a careful search.



FIGURE

Principal moments of inertia derived from a rigid rotor analysis of transitions with $J \leqslant 10$ for the normal and [^{18}O]-substituted species of cyclopent-2-en-1-one are given in the Table. The quantity, δ, defined by $\delta = I_c - I_a - I_b$ is also recorded. If the heavy atoms are coplanar one can write

$$\delta = \Delta - 2\Sigma m_i c_i^2$$

where the c_i are the out-of-plane co-ordinates of the methylenic hydrogen atoms and Δ is the inertia defect associated with the in-plane atoms. If Δ is neglected, δ can be calculated to be $-6\cdot387$ a.m.u. Å^2, using the reasonable assumed parameters $r_{\text{C–H}} = 1\cdot09$ Å and $\angle\text{HCH} = 109° 28'$

for the methylene groups. This calculated value agrees well with δ given in the Table and is strong evidence that only the methylenic hydrogen atoms are out of the plane, for δ would be significantly more negative if the other atoms had even small *c*-co-ordinates.

TABLE

*Moments of inertia (a.m.u.*Å^2*) of cyclopent*-2-*en*-1-*one*

	Normal species	$[^{18}O]$-substituted species
I_a	68·1995	68·2018
I_b	140·9172	148·959
I_c	202·7527	210·796
δ	−6·3640	−6·365

The difference between observed and calculated values of δ may be attributed to Δ, and is 0·023 and 0·022 a.m.u. Å^2 for the normal and $[^{18}O]$-species, respectively. Such a small positive quantity is consistent with the planarity of the heavy atoms.[2]

Finally, the conclusion of planarity of all but the methylenic hydrogen atoms is supported by the essential invariance of both δ and Δ on substitution of ^{18}O. The very small changes are attributed to changes in zero-point motions on isotopic substitution. Small changes of this order of magnitude are known to occur for ^{18}O-substitution in strictly planar molecules.[3] Any out-of-plane character of the oxygen atom in cyclopent-2-en-1-one would lead to large changes in δ on substitution.

One of us (D.C.) thanks the S.R.C. for a studentship and another (A.C.L.) thanks the University of London for a Turner and Newall Fellowship. Helpful advice from Dr. D. V. Banthorpe is much appreciated.

(*Received, August* 12*th,* 1969; *Com.* 1239.)

[1] C. C. Costain and S. S. Butcher, *J. Mol. Spectroscopy*, 1965, **15**, 40.

[2] T. Oka and Y. Morino, *J. Mol. Spectroscopy* (1963), **11**, 349.

[3] For example: A. C. Legon and D. J. Millen, *J. Chem. Soc.* (*A*), 1968, 1736; A. P. Cox and J. M. Riveros, *J. Chem. Phys.*, 1965, **42**, 3106.