The Microwave Spectrum of Cyclohex-2-en-1-one

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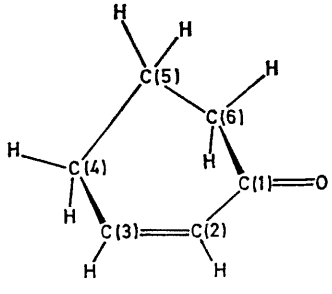
Summary The moments of inertia and non-zero value of the dipole component, μc, suggest a model for cyclohex-2-en-1-one in which all the heavy atoms are not coplanar.

A recent study of cyclopent-2-en-1-one by microwave spectroscopy[1] indicates that the heavy atom skeleton is planar. We have now observed the microwave spectrum of cyclohex-2-en-1-one and interpret the results in terms of a probable structure in which the oxygen and five of the carbon atoms are coplanar, but one of the carbon atoms [C(5)] deviates from this plane.

The spectrum was observed in the frequency range 15—32 GHz. and is dominated by μa-type transitions. All measurements were made in a 100 kHz Stark-modulated spectrometer operated at room temperature. Several vibrational satellite lines accompanied each ground-state



transition. The most prominent of these formed a very regular series of exponentially-decreasing intensities and in most cases members could be identified up to $v = 4$. Approximate relative intensity measurements on these

series of lines indicate a fundamental frequency in the region of 90 cm^{-1}. Frequencies for all ground and excited vibrational-state transitions closely followed rigid-rotor theory and the constants given in the Table were obtained by a least-squares fitting procedure based on such theory.

Stark effects were measured for several ground-state lines and the μa and μc dipole components determined as $3{\cdot}75 \pm 0{\cdot}02$D. and $0{\cdot}31 \pm 0{\cdot}01$D. respectively. No precise value of the μb component was obtained from the transitions studied. The total dipole moment in benzene solution[2] has been measured as $3{\cdot}62 \pm 0{\cdot}05$D. The non-zero value of μc suggests that not all the heavy atoms are coplanar and this suggestion is substantiated when the moments of inertia and "inertial defects" (Table) are considered.

TABLE

	A_v	B_v	C_v	I_a	I_b	I_c	Δ
$v = 0$	4770·43	2543·20	1758·29	105·9719	198·7774	287·5133	−17·2360
$v = 1$	4757·23	2546·73	1761·42	106·2658	198·5022	287·0013	−17·7667
$v = 2$	4744·15	2550·23	1764·54	106·5587	198·2294	286·4937	−18·2944
$v = 3$	4731·01	2553·69	1767·67	106·8548	197·9613	285·9872	−18·8289
$v = 4$	4717·85	2557·09	1770·78	107·1527	197·6975	285·4842	−19·3660

$\Delta = I_c - I_a - I_b$

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

For a planar configuration of the carbon and oxygen atoms the main contribution to Δ would come from the six methylenic hydrogen atoms. With reasonable values of the C–H distances and the HCH angles Δ should be in the region of −9 a.m.u.Å^2. The observed value of −17·24 a.m.u.Å^2 clearly indicates that at least one other atom is contributing to this quantity. Considerations based on molecular models suggest that, while the oxygen and five of the carbon atoms might well lie in one plane, C(5) is probably out of this plane. To test this idea moments of inertia were calculated for such a model in which the geometry of the conjugated region was based on the structure of acrolein[3] and the configurations at C(4), C(5), and C(6) were taken as approximately tetrahedral. The C(1)–C(6) and C(3)–C(4) distances were taken as 1·50 Å, and the C(4)–C(5) and C(5)–C(6) distances set at 1·54 Å. The resulting moments of inertia are (in a.m.u.Å^2): I_A = 105·40, I_B = 194·15, I_C = 280·92 and thus Δ is −18·63 a.m.u.Å^2. This last mentioned parameter is in fair agreement with the observed value and thus this rather crude model does display about the correct degree of non-planarity Seeking a model which fits the observed moments of inertia more closely does not seem justified at this stage.

We thank the S.R.C. for a maintenance grant (to S.A.M.).

(*Received, February 2nd*, 1970; *Com.* 158.)

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