The Microwave Spectra and Ring Configuration of γ-Butyrolactone and γ-Crotonolactone

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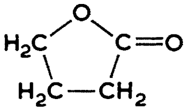
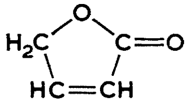
Summary The ring atoms and carbonyl oxygen atom are shown by microwave spectral studies to be coplanar in γ-crotonolactone but non-planar in γ-butyrolactone.

PREVIOUS microwave studies have shown cyclopentanone[1] to have a non-planar arrangement of the heavy atoms whereas the corresponding atoms in cyclopent-2-enone are coplanar.[2] In cyclopentanone the torsional forces about the C–C single bonds which result from eclipsed methylenic hydrogen atoms in the planar situation are sufficient to overcome the resistance of the already strained ring angles to a further decrease. The extra stability conferred on the planar configuration in cyclopent-2-enone by conjugation is, however, apparently sufficient to compensate for the torsional forces. The substitution of an oxygen atom for the 2-position methylene group of cyclopentanone leads to γ-butyrolactone (I) and the corresponding substitution in cyclopent-2-enone gives γ-crotonolactone (II). The microwave spectra of γ-butyrolactone and γ-crotonolactone have now been studied and are interpreted in terms of non-planar and planar arrangements, respectively, of the heavy atoms.



(I)



(II)

The microwave spectra of γ-butyrolactone and γ-crotonolactone both consist of strong *a*-type and weaker *b*-type transitions. Initial assignments were made from the Stark effect of *a*-type, *R*-branch transitions. A least-squares analysis of about 30 transitions with $J \leqslant 10$ for rotational constants in each case established rigid rotor behaviour in the spectra in this *J* range. The rotational constants, principal moments of inertia, and quantities $\Delta_{\text{obs}} = I_c - I_b - I_a$ for the vibrational ground states of these molecules are given in the Table.

If zero-point vibrational effects are neglected, Δ can be calculated from the relationship

$$\Delta_{\text{calc}} = -2 \sum_i m_i c_i^2$$

in which c_i is the *c*-co-ordinate of the atom *i*. When the heavy atoms are coplanar the sum extends only over the out-of-plane methylenic hydrogen atoms. The reasonable assumption of $r_{\text{C–H}} = 1{\cdot}09$ Å and ∠HCH = 109°28′ for the methylene group parameters yields the values Δ_{calc} shown in the Table if no other than the methylenic hydrogen atoms lie out of the plane.

Rotational constants (*MHz*) *and moments of inertia* (*a.m.u.*Å²)

	γ-Butyrolactone	γ-Crotonolactone
A	7279·61	8221·38
B	3585·344	3883·706
C	2562·551	2682·500
I_a	69·4233	61·4708
I_b	140·9558	130·1270
I_c	197·2156	188·3970
Δ_{obs}	−13·1635	−3·2008
Δ_{calc}	−9·580	−3·193

The small difference between Δ_{obs} and Δ_{calc} for γ-crotonolactone (which may be safely assigned to zero-point effects) is strong evidence for planarity. The large difference in the case of γ-butyrolactone can only be explained on the basis of a non-planar ring system. Moreover, the observation of a closely spaced symmetrical doublet character in high *J*,*Q*-branch transitions of γ-butyrolactone is further evidence for non-planarity. The doublet separation increases smoothly with *J* and is not resolved for $J < 20$. Such doubling is characteristic of two equivalent non-planar configurations separated by a moderately high barrier to the planar structure.

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[2] D. Chadwick, A. C. Legon, and D. J. Millen, *Chem. Comm.*, 1969, 1130.