Microwave Spectrum, Planarity, and Dipole Moment of Cyclobutane-1,2-dione

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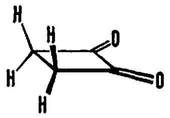
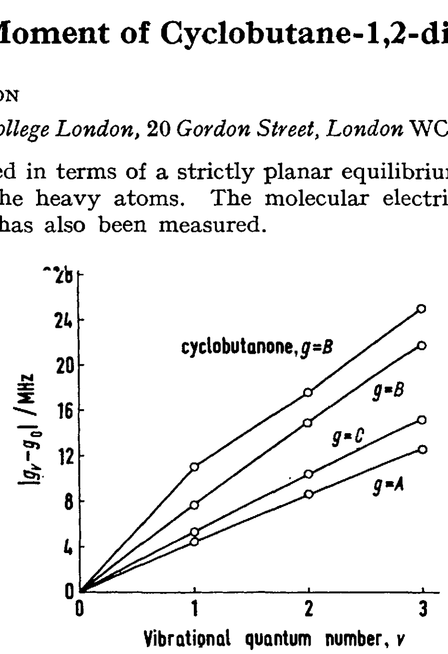
Summary The rotational spectra of cyclobutane-1,2-dione in the ground state and the first three vibrationally excited states associated with the out-of-plane ring mode establish that the heavy atoms in the molecule are coplanar; the measured electric dipole moment in the ground state is $\mu = \mu_b = 3{\cdot}82 \pm 0{\cdot}02$ D.

THE microwave spectrum of cyclobutanone[1] has been interpreted in terms of an equilibrium configuration in which the heavy atoms are almost but not quite coplanar. Indeed a barrier of only 8 cm^{-1} (lower even than the zero-point vibrational level) exists at the planar configuration, which indicates that the forces tending to pucker the ring (*e.g.* torsional forces about C–C single bonds resulting from eclipsed methylenic hydrogen atoms in the planar structure) and the forces tending to maintain planarity (*e.g.* the resistance to further decrease of strained ring angles) are delicately balanced. When one of the methylene groups adjacent to the carbonyl group of cyclobutanone is replaced by a carbonyl group to give cyclobutane-1,2-dione (**1**), a nominally sp^3 hybridised carbon atom is exchanged for on which is nominally sp^2 hybridised. Ring angle strain in th diketone therefore should be increased and the planar ring favoured relative to cyclobutanone. The microwav spectrum of cyclobutane-1,2-dione has been investigated in order to test the validity of this prediction and has been interpreted in terms of a strictly planar equilibrium structure of the heavy atoms. The molecular electric dipole moment has also been measured.



(1)



FIGURE

Cyclobutane-1,2-dione is a highly asymmetric rotor (asymmetry parameter $\kappa = 0{\cdot}1355$) exhibiting a rich rotational spectrum of μ_b-type transitions. Several low J,R branch transitions were initially identified through their Stark effects and also a characteristic, almost equally spaced vibrational satellite series (associated with the ring-puckering mode) extending to high frequency of the vibrational ground state transition. A least-squares analysis in the rigid rotor approximation for a selection of transitions with $J \leqslant 6$ indicated the effects of centrifugal distortion in the ground state and the $v = 1,2$ and 3 states of the satellite series to be negligible and yielded the rotational constants, principal moments of inertia, and quantities $\Delta_v = I_c^v - I_a^v - I_b^v$ shown in the Table.

TABLE

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

	$v = 0$	$v = 1$	$v = 2$	$v = 3$
A_v	5329·07	5333·54	5337·66	5341·53
B_v	4050·486	4042·836	4035·605	4028·728
C_v	2371·062	2376·392	2381·415	2386·207
I_a^v	94·8338	94·7543	94·6812	94·6126
I_b^v	124·7692	125·0053	125·2293	125·4431
I_c^v	213·1433	212·6652	212·2167	211·7905
Δ_v	−6·4597	−7·0944	−7·6938	−8·2652

Coplanarity of the heavy atoms in cyclobutane-1,2-dione is readily established from the spectral constants. First, Δ_0 depends only on the masses (m_H) and the out-of-plane co-ordinates (c_H) of the hydrogen atoms according to $\Delta_0 = -8m_Hc^2_H$ if zero-point vibrational effects are ignored and if the heavy atoms are coplanar. The calculated value $\Delta_0 = -6{\cdot}39$ a.m.u. Å^2 [assuming the reasonable methylenic parameters r(C–H) = 1·09 Å and ∠HCH = 109°28′] agrees closely with the experimental value and suggests a planar heavy atom configuration. However, such arguments cannot rule out a very small degree of non-planarity at equilibrium.[2]

Unambiguous evidence of planarity is contained in the smooth variation of the rotational constants $g_v - g_0$ (where $g = A$, B, or C) as a function of the vibrational quantum number, v, of the satellite series (Figure). That the vibration involves heavy atoms moving out-of-plane is established by the increasingly more negative values of Δ_v as v increases. The smooth curvature of the rotational constants of cyclobutane-1,2-dione is to be compared (Figure) with the distinct zig-zag behaviour of $B_v - B_0$ *vs.* v for the ring-puckering mode of cyclobutanone.[1] In the latter molecule, the tiny barrier to the planar ring suffices to perturb the $v = 0$, 1, and 2 states differentially and leads to the zig-zag of the rotational constants even though it is lower than the $v = 0$ level. In cyclobutane-1,2-dione, however, the smooth variation is indicative of a single minimum potential function[3] and therefore coplanar heavy atoms at equilibrium.

The dipole moment of cyclobutane-1,2-dione (restricted to a non-zero value for only μ_b by the established planarity and the observed transition type) was measured using the $M = 1$ and $M = 2$ Stark components of the $3_{3,1} - 2_{2,0}$ and $3_{1,3} - 2_{0,2}$ ground-state transitions to give values of $\mu = \mu_b = 3{\cdot}83$, $3{\cdot}85$, $3{\cdot}80$, and $3{\cdot}81$ Debye respectively. The $J = 2 \leftarrow 1$ and $J = 1 \leftarrow 0$ transitions of propyne[4] were used to calibrate the absorption cell.

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