Determination of a High Potential Barrier Hindering Internal Rotation in 2-Methylcyclopentanone and α-Methyl-γ-Butyrolactone by Microwave Fourier Transform Spectroscopy

J. L. Alonso[1,2], N. Heineking, and H. Dreizler

Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel,
Kiel, F. R. Germany

A. G. Lesarri and J. C. López

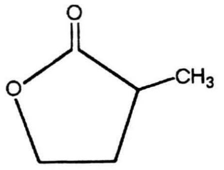
Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid,
47005 Valladolid, Spain

Z. Naturforsch. **47a,** 761–764 (1992); received March 28, 1992

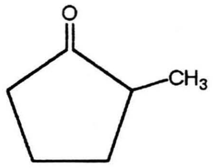
The microwave spectra of α-methyl-γ-butyrolactone and 2-methylcyclopentanone have been reinvestigated using microwave Fourier transform spectroscopy. $A-E$ splittings due to internal rotation of the methyl group have been observed in the ground and several vibrationally excited states for both molecules. From an internal-axis-method analysis of these splittings, values of the methyl group internal rotation barrier of 2.61 kcal mol^{-1} for α-methyl-γ-butyrolactone and 2.41 kcal mol^{-1} for 2-methylcyclopentanone have been obtained.

It has already been demonstrated that the value of the barrier to internal rotation determined from $A-E$ line splittings in the ground state is the most reliable one if the measuring accuracy is sufficient [1]. This is related to the fact that interaction terms in the rotation-torsion-vibration Hamiltonian lead to noticeable effects if there is a near degeneracy between torsional and vibrational levels [2–4]. Such a degeneracy generally does not include the ground state. Its $A-E$ torsional splitting is therefore a rather reliable source of information.

We have investigated the microwave spectra of the methylcycloderivatives 2-methyl-4,5-dihydrofuran [5], α-angelicalactone [6] and 3-methylcyclopent-2-enone [7]. In these studies we found differences between the $A-E$ splittings observed in the ground and excited states of the ring-puckering vibration (compare [5], Tab. V, and [6], Tab. IV). This indicates the existence of some interaction between the methyl torsion and ring-puckering vibration for these molecules.



(I)



(II)

In previous papers we reported an analysis of the rotational spectra of 2-methylcyclopentanone [8] (II) and α-methyl-γ-butyrolactone [9] (I). A ring-twisted-like conformation in which the methyl group is in the equatorial position was found for both molecules. $A-E$ splittings were not observed within the resolution of our computer-controlled Stark modulation spectrometer [9]. For this reason, and to investigate the possibility of the determination of the high barriers from the splittings of rotational transitions in the ground state we decided to reanalyse the rotational spectra of these molecules using microwave Fourier transform (MWFT) spectroscopy. This technique provides sensitivity and resolution high enough to search for internal rotation splittings in the ground and excited states. This investigation would give in addition also hints for an interaction between ring-puckering and methyl torsion.

The MWFT spectrometer used in this work has been described elsewhere [10]. Samples of 2-methylcyclopentanone and α-methyl-γ-butyrolactone were purchased from ICI Chemicals and Aldrich Chemical Co., and used without further purification. Temperature was about −50 °C and pressure down to 1 mTorr.

---

[1] Permanent Address: Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain.

[2] Alexander-von-Humboldt-Stiftung fellow 1990.

Reprint requests to Prof. Dr. H. Dreizler, Institut für Physikalische Chemie, Universität Kiel, Olshausenstraße 40, W-2300 Kiel 1.

0932-0784 / 92 / 0600-0761 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. Observed frequencies and $E-A$ splittings and differences between the observed and calculated splittings (in MHz) for the ground and excited states of α-methyl-γ-butyrolactone.

Transition $J'_{k'_{-1}k'_{+1}} \leftarrow J''_{k''_{-1}k''_{+1}}$	Ground state			$v_\alpha=1$			$v_\alpha=2$			$v_\beta=1$			$v_\gamma=1$		
	Freq.[a]	Splittings		Freq.[a]	Splittings		Freq.[a]	Splittings		Freq.[a]	Splittings		Freq.[a]	Splittings	
		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]
$19_{12,7} \leftarrow 19_{12,8}$	9171.370	0.032	−0.009												
$21_{13,8} \leftarrow 21_{13,9}$	12239.449	0.061	0.011	12726.274	0.057	0.006									
$22_{14,8} \leftarrow 22_{14,9}$	8799.295	0.045	−0.005							9143.675	0.046	–[b]			
$24_{15,9} \leftarrow 24_{15,10}$	11855.976	0.061	−0.001												
$25_{16,9} \leftarrow 25_{16,10}$	8251.974	0.060	0.002	8834.313	0.064	0.003							8622.051	0.075	–[b]
$27_{17,10} \leftarrow 27_{17,11}$	11251.809	0.070	−0.002	11979.443	0.065	−0.009				11757.203	0.073	–[b]			
$28_{18,10} \leftarrow 28_{18,11}$				8239.214	0.067	0.000									
$30_{19,11} \leftarrow 30_{19,12}$	10479.435	0.082	0.002	11312.382	0.079	−0.004	12182.969	0.072	−0.018				11001.910	0.086	–[b]
$31_{20,11} \leftarrow 31_{20,12}$							8318.230	0.081	0.001						
$33_{21,12} \leftarrow 33_{21,13}$	9591.570	0.087	0.001	10510.896	0.093	0.002									
$35_{22,13} \leftarrow 35_{22,14}$	12903.486	0.102	−0.002												
$36_{23,13} \leftarrow 36_{23,14}$	8638.708	0.086	−0.002				10677.538	0.111	0.005						
$38_{24,14} \leftarrow 38_{24,15}$	11797.343	0.113	0.003												
$39_{25,14} \leftarrow 39_{25,15}$							9798.911	0.119	0.004						

[a] Frequencies for the A-species. – [b] Calculated from parameters of Table 3. – [c] Non fitted data.

Table 2. Observed frequencies and $E-A$ splittings and differences between the observed and calculated splittings (in MHz) for the ground and excited states of 2-methylcyclopentanone.

Transition $J'_{k'_{-1}k'_{+1}} \leftarrow J''_{k''_{-1}k''_{+1}}$	Ground state			$v_\alpha=1$			$v_\alpha=2$			$v_\beta=1$			$v_\gamma=1$		
	Freq.[a]	Splittings		Freq.[a]	Splittings		Freq.[a]	Splittings		Freq.[a]	Splittings		Freq.[a]	Splittings	
		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]		Obs.	Obs.-cal.[b]
$17_{10,7} \leftarrow 17_{10,8}$	9998.968	0.044	0.001	10155.519	0.052	0.005				10112.889	0.043	0.001			
$19_{11,8} \leftarrow 19_{11,9}$	12458.615	0.052	−0.001	12648.383	0.055	−0.002	12843.236	0.060	0.005						
$20_{12,8} \leftarrow 20_{12,9}$	8905.497	0.059	0.004	9113.529	0.057	−0.003				9051.915	0.061	0.008			
$22_{13,9} \leftarrow 22_{13,8}$	11246.828	0.065	−0.002	11500.860	0.070	−0.003	11762.998	0.078	0.007						
$25_{15,10} \leftarrow 25_{15,11}$	9728.857	0.086	0.008	10034.753	0.085	0.000	10352.763	0.081	−0.003	9939.946	0.076	0.001			
$27_{16,11} \leftarrow 27_{16,12}$	12177.686	0.095	0.003	12543.837	0.102	0.002	12922.723	0.103	0.005	12430.825	0.086	−0.003			
$28_{17,11} \leftarrow 28_{17,12}$	8072.260	0.073	−0.009	8409.237	0.088	−0.003	8763.005	0.099	0.008	8301.229	0.081	0.001	8493.739	0.037	–[c]
$30_{18,12} \leftarrow 30_{18,13}$	10300.592	0.102	0.002	10713.312	0.111	0.001	11144.425	0.102	−0.007	10581.443	0.093	−0.003	10819.519	0.044	–[c]
$32_{19,13} \leftarrow 32_{19,14}$	12836.770	0.124	0.007												
$33_{20,13} \leftarrow 33_{20,14}$	8382.761	0.093	−0.008	8813.939	0.112	0.001				8672.391	0.106	0.009			
$35_{21,14} \leftarrow 35_{21,15}$	10659.206	0.118	−0.004	11184.026	0.127	−0.006	11735.432	0.126	−0.007	11012.044	0.113	−0.004	11302.403	0.061	–[c]
$38_{23,15} \leftarrow 38_{23,16}$	8535.181	0.118	0.002	9061.097	0.137	0.007				8884.882	0.109	−0.003			

[a] Frequencies for the A-species. – [b] Calculated from parameters of Table 4. – [c] Non-fitted data.

Table 3. Parameters from IAM analysis of the ground and excited states of α-methyl-γ-butyrolactone (v_α, ring-puckering motion, v_β and v_γ vibrationally unassigned states).

	Ground state	$v_\alpha=1$	$v_\alpha=2$
I_α[a] (AMU Å^2)	[3.19][h]		
F[b] (GHz)	[162.5]		
ϱ[c]	[0.020]		
β[d] (rad)	[0.4242]		
γ[e] (rad)	[0.7559]		
s[f]	74.9 (9)[i]	74.9 (3)	74.5 (5)
V_3[g] (cal mol^{-1})	2611 (7)	2612 (10)	2598 (18)

[a] Moment of inertia of the methyl group.

[b] Reduced internal rotation constant.

[c] $\varrho = |\varrho|,\ \vec{\varrho} = \lambda_a \frac{I_\alpha}{I_a},\ \lambda_b \frac{I_\alpha}{I_b},\ \lambda_c \frac{I_\alpha}{I_c};$

λ_g, $g = a, b, c$ direction cosine connecting internal rotation and inertia axes,

I_g, $g = a, b, c$ moments of inertia.

The following I_g and λ_g values have been derived from a twisted equatorial assumed structure

$I_a = 140.295$ AMU Å^2, $\lambda_a = 0.8116$,
$I_b = 161.831$ AMU Å^2, $\lambda_b = -0.3076$,
$I_c = 277.145$ AMU Å^2, $\lambda_c = -0.4966$.

[d] Euler angle between a axis and $\vec{\varrho}$, $\beta = \arccos \frac{\lambda_a I_\alpha}{I_a \varrho}$

[e] Euler angle $\gamma = \arccos \left(\frac{\lambda_b I_\alpha}{I_b \sqrt{\left(\frac{\lambda_b I_\alpha}{I_b}\right)^2 + \left(\frac{\lambda_c I_\alpha}{I_c}\right)^2}} \right)$

can be derived from [15].

[f] Reduced barrier height $s = 4 \frac{V_3}{9F}$.

[g] Barrier height.

[h] Fixed in square brackets from the structure for all states.

[i] Standard errors in units of the last digit. They do not reflect the errors introduced by the assumed structure.

Table 4. Parameters from IAM analysis of the ground and excited states of 2-methylcyclopentanone. See also Table 3.

	Ground state	$v_\alpha=1$	$v_\alpha=2$	$v_\beta=1$
I_α[a] (AMU Å^2)	[3.19][b]			
F (GHz)	[162.4]			
ϱ	[0.019]			
β (rad)	[0.4792]			
γ (rad)	[0.6170]			
s	69.2 (2)	68.7 (2)	68.9 (3)	69.3 (2)
V_3(cal mol^{-1})	2412 (7)	2394 (7)	2401 (10)	2415 (7)

[a] See Table 3 for definition of parameters.

[b] Fixed in square brackets from the assumed structure for all states.

The following I_g and λ_g values have been derived from this structure.

$I_a = 144.407$ AMU Å^2, $\lambda_a = 0.7886$,
$I_b = 170.859$ AMU Å^2, $\lambda_b = -0.3954$,
$I_c = 286.893$ AMU Å^2, $\lambda_c = -0.4709$.

As the spectra had already been assigned and the published constants [8, 9] gave a good prediction, the measurements could easily be extended to the 8–13 GHz frequency range. After a precise search at very low pressures, internal rotation splittings were observed in some rotational transitions of the ground and excited states for both molecules. The frequencies of the narrow splitted lines were determined by a time domain fit procedure [11]. The frequencies for the A states and the corresponding splittings are reported in Tables 1 and 2. They have been fitted for each vibrational state separately by using the internal axis method (IAM) [12–14] in the form of the high barrier approximation of the Woods program (INTROT) [15, 16]. As the splittings were only slightly dependent on ϱ, β and γ, these parameters were constrained to the values arising from the structural model, and only the reduced barrier s was determined from the experimental splittings. For α-methyl-γ-butyrolactone a twisted equatorial structure has been assumed [9]. For 2-methylcyclopentanone a twisted equatorial structure has been assumed [8], based on the reported structure of cyclopentanone [17] with all $CH = 1.095$ Å and $HCH = 109.5°$, the CHC and CH_3-C-H planes and the carbonyl $C=O$ bond taken to bisect the corresponding ring angles and a ring-twisting angle of 21°. The obtained results are shown in Tables 3 and 4 along with the other parameters relevant to the internal rotation of the methyl group.

The energy separation for the methyl torsion states $v_t = 0$ and $v_t = 1$ has been calculated from the tables of torsional energy levels [18] to be 198 cm^{-1} and 191 cm^{-1} for α-methyl-γ-butyrolactone and 2-methylcyclopentanone, respectively.

The nearly equal $A-E$ splittings observed for the same rotational transitions in the ground and the vibrational excited states of the ring-puckering motion ($v_\alpha=1$, $v_\alpha=2$) indicates a very small interaction, at most, between ring-puckering and methyl torsion vibrations. This might be expected if we consider that the $v_\alpha = 1-0$ energy spacings for the ring-puckering vibrations of α-methyl-γ-butyrolactone and 2-methylcyclopentanone obtained from relative intensity measurements are ~132 cm^{-1} and ~87 cm^{-1}, respectively. Only the three splittings observed in the $v_\gamma = 1$ state of 2-methylcyclopentanone are significantly smaller than those observed on the same lines of the ground state, which is an indication that this state is influenced by another vibration.

On the basis of the $A-E$ splittings observed in the states $v_\beta = 1$ and $v_\gamma = 1$ it can be definitively excluded that these states belong to the first methyl torsion excited state. This assumption was made in previous works [8, 9], in which a false lower limit for the barrier of ~ 3.5 kcal mol^{-1} was proposed.

According to [1], the most reliable value for the internal rotation barrier is that obtained from rotational transitions in the ground state. The nearly similar values obtained for both molecules can be understood by realizing that the close environment of the methyl group is the same for both molecules.

Acknowledgements

Funds from the Deutsche Forschungsgemeinschaft, Fonds der Chemie and the Land Schleswig-Holstein are gratefully acknowledged. J. L. A. thanks the Von Humboldt Foundation for financial support.

[1] H. Dreizler, in: Molecular Spectroscopy: Modern Research, Vol. I, p. 59, K. N. Rao and C. W. Mathews, eds., Academic Press, New York 1972.
[2] H. Mäder, U. Andresen, and H. Dreizler, Z. Naturforsch. **28a**, 1163 (1973).
[3] H. Mäder, H. M. Heise, and H. Dreizler, Z. Naturforsch. **29a**, 164 (1974).
[4] U. Andresen and H. Dreizler, Z. Naturforsch. **29a**, 797 (1974).
[5] J. L. Alonso, J. C. López, R. Cervellati, and D. G. Lister, J. Mol. Spectrosc. **112**, 26 (1985).
[6] J. L. Alonso, F. L. Peláez, J. C. López, D. G. Lister, and R. Cervellati, J. Mol. Spectrosc. **124**, 199 (1987).
[7] F. J. Peláez, J. C. López,, and J. L. Alonso, J. Mol. Struct. **159**, 19 (1987).
[8] J. L. Alonso, J. C. López, and R. M. Villamañán, J. Mol. Spectrosc. **126**, 348 (1987).
[9] J. C. López, J. L. Alonso, and F. J. Pelaéz, J. Mol. Spectrosc. **131**, 9 (1988).
[10] M. Krüger and H. Dreizler, Z. Naturforsch. **45a**, 724 (1990).
[11] J. Haekel and H. Mäder, Z. Naturforsch. **43a**, 203 (1988).
[12] K. T. Hecht and D. M. Denninson, J. Chem. Phys. **26**, 31 (1957).
[13] L. C. Lin and I. D. Swalen, Rev. Mod. Phys. **31**, 84 (1959).
[14] H. Dreizler, Fortschr. Chem. Forsch. **10**, 59 (1968).
[15] R. C. Woods, J. Mol. Spectrosc. **21**, 4 (1966).
[16] R. C. Woods, J. Mol. Spectrosc. **22**, 49 (1967).
[17] A. Kh. Mamleev, L. N. Gunderova, and N. H. Pozdeev, Zh. Struckt. Khim. **19**, 744 (1978).
[18] D. R. Herschbach, "Tables for the internal rotation problem". Department of Chemistry, Harvard University, Cambridge, Mass. 1957, J. Chem. Phys. **27**, 975 (1957).