Microwave Spectrum of γ-Thiobutyrolactone

José L. Alonso, J. C. Lopez, and F. Mata
Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid,
Valladolid, Spain

Z. Naturforsch. **37a**, 129–133 (1982); received November 7, 1981

The microwave spectrum of γ-thiobutyrolactone has been observed and measured in the vibrational ground state and in several excited states of the ring-bending and ring-twisting modes. From the value of the μ_c component of the dipole moment and inertial-defect considerations the ring skeleton was shown to be non-planar. The average intensity ratio for the rotational transitions between the ground and excited vibrational states indicates that the first excited state of the ring-bending and ring-twisting modes are $\sim 120\ \mathrm{cm}^{-1}$ and $\sim 250\ \mathrm{cm}^{-1}$ above the ground state respectively. These two out-of-plane ring vibrations are essentially independent and the ring-bending vibration is governed by a nearly harmonic potential energy function. The components of the dipole moment were determined by the Stark effect to be $\mu_a = 3.770 \pm 0.001$ D, $\mu_b = 1.818 \pm 0.044$ D and $\mu_c = 0.832 \pm 0.018$ D, leading to $\mu_{\text{total}} = 4.268 \pm 0.023$ D. The rigidity of the γ-thiobutyrolactone ring is discussed in relation to those of related molecules.

Introduction

Saturated five-membered rings have two low-frequency, out-of-plane ring modes, a twisting and a bending vibration which may be coupled in some cases to produce a resultant motion in which the ring vibrates so that the location of its puckering rotates about the ring and the nature of the puckering alternates between bending and twisting. The name pseudorotation has been given to this type of vibrational motion [1, 2].

Pitzer and Donath [3] predict hindered pseudorotation in any saturated five-membered ring in which the skeletal torsional barriers are not all equivalent. Thus, the presence of a barrier to pseudorotation has been used to explain the microwave spectra of several five-membered ring [4–8]. In molecules with sufficiently high barriers, the motion can be treated as an ordinary vibration in which the puckering oscillates about a most stable configuration. Such high barriers would negate the effects of pseudorotation on the microwave spectrum. Thus, it is established that cyclopentanone [6] and methylenecyclopentane [7] have a permanently twisted equilibrium conformation and undergoing bending and twisting vibration quite independently. The lower limit to the height of barrier to pseudorotation in cyclopentanone was set 400 cm^{-1}.

In the light of the above information we have investigated the microwave spectrum of γ-thiobutyrolactone (see Fig. 1) in order to determine the stable configuration and establish the nature and frequencies of the low-frequency out-of-plane ring modes. In a preliminary publication [9] it was shown that the ground state rotational constants of γ-thiobutyrolactone are consistent with an equilibrium ring conformation in which the heavy atoms are non-planar. We now report a full analysis of the microwave spectrum in the ground state and in excited states of the ring-bending and ring-twisting modes.

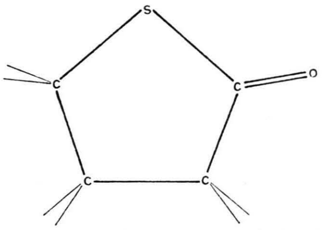

Fig. 1. The γ-thiobutyrolactone molecule.

Two review papers [10, 11] have recently been published which give an extensively illustrated discussion of the low-frequency vibrations of small ring molecules.

Experimental

The sample γ-thiobutyrolactone was obtained from Pfaltz and Bauer and used without further purification. Microwave spectra were recorded using a

---

Reprint requests to Dr. J. L. Alonso, Departamento de Química-Física, Facultad de Ciencias, Universidad de Valladolid, Valladolid, España.

0340-4811 / 82 / 0200-0129 $ 01.30/0. — Please order a reprint rather than making your own copy.

Hewlett-Packard model 8460 A MRR microwave spectrometer with a Stark modulation frequency of 33.3 kHz. The spectrum was studied in the K-band region (18.0 to 26.5 GHz). The frequency accuracy was estimated to be better than ± 0.05 MHz. In order to condition the Stark cell, the sample was flowed through the cell. Once the Stark cell was conditioned, spectra of the static sample could be obtained for a short period of time before resampling was necessary. In the determination of the electric dipole moment, all ground-to-base voltage measurements were made using an HP-34698 digital voltmeter. All observations were taken at room temperature with sample pressures in the range $10-30\,\mu$.

Rotational Spectra

γ-Thiobutyrolactone is an asymmetric rotor ($K = -0.04$) in which the a-type transitions were expected to be dominant. A survey scan of the spectrum did not provide any prominent characteristics. However, for a-type R-branch transitions of a highly asymmetric rotor, the transitions $(J+1)_{0,J+1} \leftarrow J_{0,J}$ and $(J+1)_{1,J+1} \leftarrow J_{1,J}$ turn out to be nearly coincident in frequency, and are expected to be comparatively strong. This fact, along with the characteristic mirror image Stark effect which these transitions possess, indicated that these lines would be the most useful in the initial search. Thus, the pairs of transitions $5_{0,5} \leftarrow 4_{0,4}$, $5_{1,5} \leftarrow 4_{1,4}$ and $6_{0,6} \leftarrow 5_{0,5}$, $6_{1,6} \leftarrow 5_{1,5}$ were readily assigned. After a-type R-branch assignments were made, it was quite simple to locate the b-type transitions $(J+1)_{1,J+1} \leftarrow J_{0,J}$, $(J+1)_{0,J+1} \leftarrow J_{1,J}$ which were also nearly coincident in frequency. Initial rotational constants, determined from a least-squares analysis of low J in the rigid-rotor approximation allowed a- and b-type Q-branch transitions to be assigned. c-type transitions are much weaker in intensity and it was possible to measure only a few of them precisely because of the high density of the spectrum.

A vibrational satellite series, with several members observable, accompanies each R-branch transition to the high frequency side and was assigned, by analogy with that of similar molecules [6, 7], to successive quanta of the ring-bending vibration v_b. This series proceeds to increase in frequency and decrease in intensity in a regular fashion and the mode seems to be fairly harmonic. Another vibrational satellite, which falls on the low-frequency side of the ground state, was assigned to the first excited state of the ring-twisting mode v_t. The assignment was facilitated by the Stark effect pattern and is supported by a progressively more negative value of Δ_v as v increases (see Table 1), a behaviour characteristic of such vibrations [12].

Rotational constants and quartic centrifugal distortion constants were determined for each vibrational state from all measured lines having $J < 30$ using a centrifugal distortion analysis according to Watson [13, 14]. Because the distortion contributions are very small, only first order contributions

Table 1. Rotational constants (MHz), principal moments of inertia (a.m.u. Å^2)[a] and centrifugal distortion coefficients (kHz) for the ground state and excited states of the ring-bending and ring-twisting vibration of γ-thiobutyrolactone.

	Ground State	$v_b = 1$	$v_b = 2$	$v_b = 3$	$v_t = 1$
A	4448.784 ± 0.004	4438.341 ± 0.005	4428.525 ± 0.006	4419.043 ± 0.010	4443.915 ± 0.006
B	3143.310 ± 0.004	3144.416 ± 0.005	3145.444 ± 0.006	3146.498 ± 0.009	3140.874 ± 0.006
C	1948.570 ± 0.004	1950.347 ± 0.005	1951.946 ± 0.006	1953.517 ± 0.009	1945.949 ± 0.006
K	− 0.044289	− 0.040135	− 0.036172	− 0.032271	− 0.043282
I_a	113.5987 ± 0.0001	113.8660 ± 0.0001	114.1184 ± 0.0002	114.3632 ± 0.0003	113.7231 ± 0.0002
I_b	160.7783 ± 0.0002	160.7217 ± 0.0002	160.6692 ± 0.0003	160.6154 ± 0.0005	160.9030 ± 0.0003
I_c	259.3574 ± 0.0006	259.1210 ± 0.0006	258.9088 ± 0.0008	258.7006 ± 0.0012	259.7067 ± 0.0007
$\Delta_v = I_c - I_a - I_b$	− 15.0196 ± 0.0003	− 15.4667 ± 0.0003	− 15.8788 ± 0.0004	− 16.2780 ± 0.0006	− 14.9195 ± 0.0004
Δ_J	0.245 ± 0.080	0.241 ± 0.089	0.069 ± 0.106	0.172 ± 0.168	0.302 ± 0.104
Δ_{JK}	0.315 ± 0.029	0.259 ± 0.030	0.397 ± 0.041	0.348 ± 0.096	0.381 ± 0.067
Δ_K	0.666 ± 0.032	0.695 ± 0.031	0.509 ± 0.044	0.608 ± 0.097	0.624 ± 0.070
δ_J	0.069 ± 0.003	0.062 ± 0.004	0.077 ± 0.005	0.075 ± 0.011	0.077 ± 0.008
δ_K	0.350 ± 0.020	0.382 ± 0.021	0.295 ± 0.027	0.335 ± 0.063	0.305 ± 0.044
N[b]	125	84	71	49	55
S[c]	0.057	0.041	0.046	0.073	0.057

[a] Conversion factor: $I_a = 5.05376\ 10^5/A$.

[b] Number of lines fitted.

[c] Standard deviation of the calculation.

Table 2. Correlation matrix for the ground state.

A	1.000							
B	0.971	1.000						
C	0.929	0.977	1.000					
Δ_J	0.907	0.945	0.954	1.000				
Δ_{JK}	0.148	0.097	− 0.071	− 0.025	1.000			
Δ_K	− 0.047	0.093	0.016	− 0.007	− 0.851	1.000		
δ_J	0.171	0.093	− 0.089	− 0.037	0.972	− 0.712	1.000	
δ_K	− 0.164	0.094	0.079	0.030	− 0.965	0.705	− 0.922	1.000

Table 3. Relative Intensities of Vibrational Satellites in γ-Thiobutyrolactone.

Transition	Number of transitions	Average rel. intensity	Vibrational separation cm^{-1}
$v_b = 1 \leftarrow 0$	11	0.56 (0.02)[a]	120 ± 17
$v_b = 2 \leftarrow 1$	7	0.55 (0.02)	124 ± 17
$v_b = 3 \leftarrow 2$	5	0.55 (0.04)	124 ± 20
$v_t = 1 \leftarrow 0$	7	0.30 (0.01)	250 ± 15

[a] Numbers in parentheses are standard deviations.

Table 4. Stark coefficients $[\mathrm{MHz}/(\mathrm{V/cm})^2]$ and dipole moment of γ-thiobutyrolactone.

Transition	$\lvert M \rvert$	$(\Delta\nu/E^2) \times 10^5$ Obs.[a]	Calc.
$4_{2,3} \leftarrow 3_{2,2}$	0	0.383 (0.006)	0.382
	1	3.652 (0.017)	3.664
	2	13.51 (0.12)	13.51
$4_{2,2} \leftarrow 3_{2,1}$	0	0.290 (0.002)	0.291
	1	− 3.251 (0.015)	− 3.250
$5_{3,3} \leftarrow 4_{3,2}$	0	0.330 (0.004)	0.329
	1	6.566 (0.021)	6.530
	2	25.12 (0.13)	25.128
$5_{2,4} \leftarrow 4_{2,3}$	0	0.113 (0.002)	0.117

	Correlation Coefficients		
$\mu_a = 3.770\ (0.001)$[a] D	1.0000		
$\mu_b = 1.818\ (0.044)$ D	0.2178	1.0000	
$\mu_c = 0.832\ (0.023)$ D	− 0.5355	0.0026	1.0000
$\mu_{\text{total}} = 4.268\ (0.023)$ D			

[a] The uncertainties are standard deviations.

were needed. The spectroscopic constants resulting from the least-squares fit are given in Table 1. Clearly good values have been obtained. Tables containing measured transition frequencies and assignments, along with the difference from those calculated by using the constants of Table 1, and the distortion contributions may be obtained from the authors on request.

The vibrational separation for the lower states in the ring-bending and ring-twisting modes may be obtained from relative intensity measurements within the v_b and v_t vibrational satellite progressions, respectively. The microwave relative intensity measurements were carried out by the method of Esbitt and Wilson [15] and the results are recorded in Table 3.

Dipole Moment

With the possibility of three nonzero components of the dipole moment, it was necessary to measure the Stark displacements for nine components belonging to four rotational transitions. All these components were observed to have a strictly second-order Stark effect. The calculation of the necessary Stark coefficients was accomplished by the method of Golden and Wilson [16]. The electric field was calibrated using the $M = 0$ and $\lvert M \rvert = 1$ components of the $2 \leftarrow 1$ of OCS. The dipole moment of OCS was taken as 0.71521 D [17]. The transitions used, $\lvert M \rvert$ components, second-order Stark coefficients and values of the dipole moment components are given in Table 4. The calculated values of the Stark coefficients represent those calculated employing dipole components obtained from a least-squares fit to all the measured displacements.

Discussion

The experimental rotational constants listed in Table 1 give $\Delta = I_c - I_a - I_b$ in the ground state as -15.0196 amu Å^2 which must contain an appreciable contribution from the heavier atom skeleton [9]. Consequently, we may conclude that the molecule of γ-thiobutyrolactone has a non-planar ring conformation. An identical conclusion may also be reached from the result of the Stark study. If the skeletal ring is non-planar, the dipole moment will have a component in the near out-of-plane direction. The pronounced effect of the μ_c dipole on the Stark

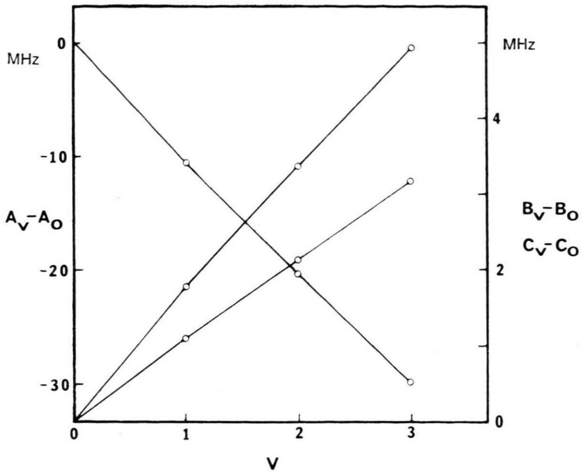

Fig. 2. Variation of the rotational constants with increasing quantum number of the ring-bending mode.

shifts of the a-type transitions used in the calculation makes it possible to give a confident value of 0.832 ± 0.018 D. Thus, the nonzero value of μ_c gives further support for the non-planar ring structure.

As shown in Table 1, the semi-rigid rotor behaviour indicates that there was no observable mixing between any pair of vibrational levels of the out-of-plane modes. Also, the near linearity of the plots in Fig. 2 seems to indicate that the ring-bending mode is fairly harmonic. It leads us to believe that the barrier to pseudorotation becomes large and the molecule undergoes both a twisting and bending motion independently about the most stable puckered conformation. However, it is not possible to determine from our microwave data whether the most stable form is the bent or the twisted conformation. Pitzer and Donath [3] have shown that certain torsional parameters evaluated for cyclopentane may be transferred to derivatives to predict the energy difference, ΔV_c, for the conformation change from the bent to the twisted form. Thus, negative values for ΔV_c have been obtained for cyclopentanone, methylencyclopentane, thiacyclopentane and γ-butyrolactone [3, 18] which indicate that the twisted form would be the stable one in good agreement with experimental results. For γ-thiobutyrolactone, although there is not enough torsional information, a similar behaviour is expected, so the twisted conformation should be the more stable one.

Since the transitions of the highest vibrational state measured show no measurable splitting, we can set the lower limit of the barrier to pseudorotation to be about 360 cm^{-1}. With a pseudorotational constant $B = 2.1\ \mathrm{cm}^{-1}$ [19] and the frequency 120 cm^{-1} of the $1 \leftarrow 0$ transition of the ring-bending vibration, a higher limit for the two-fold barrier to pseudorotation is calculated to be $\sim 2700\ \mathrm{cm}^{-1}$ using the one-dimensional approximation [20]. Previous calculations [18, 21, 22] show that one-dimensional approximations lead to values which are about 30 per cent higher than those obtained by two-dimensional treatments. Taken this into account a higher limit for the barrier of $\sim 1750\ \mathrm{cm}^{-1}$ is predicted.

It has been established by a two-dimensional treatment that the interconversion between equivalent C_2 forms in cyclopentanone [21] is most facile through the planar ring with a barrier of $\sim 750\ \mathrm{cm}^{-1}$. This smaller barrier to planarity than cyclopentane of $\sim 1930\ \mathrm{cm}^{-1}$ [23] is consistent with the increased angle strain in the planar ring and reduced torsional barrier about CH_2-CO bonds [11]. Also, the barrier to the torsional motion about C-S bonds in thiacyclopentane [24] is considerably lower than that about C-C ring bonds so the energy required to invert the conformation via pseudorotation is higher than that required for direct inversion through the planar ring. If, by analogy with these molecules, the γ-thiobutyrolactone has a twisted conformation, the most facile route to inversion should be through the planar ring.

In γ-thiobutyrolactone, the ring angle strain is reduced relative to γ-butyrolactone because the open-chain angle $\sphericalangle$ CSC (98° 52′ in dimethylsulfide [25]) is smaller than the corresponding $\sphericalangle$ COC angle (111° 43′ in dimethyl ether [26]). Hence the torsional forces are more significant in γ-thiobutyrolactone and the barrier to planarity is greater than in γ-butyrolactone. Thus, the microwave spectrum of γ-butyrolactone [18] shows inversion doubling at very high J transitions of the ground state while in ethylene carbonate [27] all ground state and excited state rotational transitions show the effect of a low barrier. This seems to indicate that a progressive substitution of CH_2 by O or S appears to lower the energy barrier. Thus, in comparison with these related molecules, we have to conclude that the γ-thiobutyrolactone molecule has a sufficiently high barrier and the ring is not significantly different in rigidity than those of cyclopentanone and methylenecyclopentane.

[1] D. O. Harris, G. G. Engerholm, C. A. Tolman, A. C. Luntz, R. A. Keller, H. Kim, and W. D. Gwinn, J. Chem. Phys. **50**, 2438 (1969).
[2] J. Laane, Vibrational Spectra and Structure, J. R. Durig, Ed., Marcel Dekker Inc. New York 1972, Vol. 1, Chapter 2.
[3] K. S. Pitzer and W. E. Donath, J. Amer. Chem. Soc. **81**, 3213 (1959).
[4] G. G. Engerholm, A. C. Luntz, and W. D. Gwinn, J. Chem. Phys. **50**, 2446 (1969).
[5] P. A. Baron and D. O. Harris, J. Mol. Spectrosc. **49**, 70 (1974).
[6] H. Kim and W. D. Gwinn, J. Chem. Phys. **57**, 1896 (1969).
[7] J. R. Durig, Y. S. Li, and L. A. Carreira, J. Chem. Phys. **57**, 1896 (1972).
[8] J. L. Alonso, J. Mol. Struct. **73**, 71 (1981).
[9] J. L. Alonso, J. C. S. Chem. Comm. 577 (1981).
[10] L. A. Carreira, R. C. Lord, and T. B. Malloy, Jr., Top. Curr. Chem. **82**, 1 (1979).
[11] A. C. Legon, Chem. Rev. **80**, 231 (1980).
[12] K. Kuchitsu, T. Oka, and Y. Morino, J. Mol. Spectrosc. **15**, 51 (1965).
[13] J. K. G. Watson, J. Chem. Phys. **46**, 1935 (1967).
[14] J. K. G. Watson, in "Vibrational Spectra and Structure", J. R. Durig Ed., Elsevier, Amsterdam 1977, p. 1.
[15] A. S. Esbitt and E. B. Wilson, Rev. Sci. Instrum. **34**, 901 (1963).
[16] S. Golden and E. B. Wilson, J. Chem. Phys. **16**, 669 (1948).
[17] J. S. Muenter, J. Chem. Phys. **48**, 4544 (1968).
[18] J. R. Durig, Y. S. Li, and C. C. Tong, J. Mol. Struct. **18**, 269 (1973), and A. C. Legon, J. C. S. Chem. Comm. **1970**, 838.
[19] Transferred from the average value of cyclopentanone (1.93 cm^{-1}) and thiacyclopentane (2.35 cm^{-1}).
[20] J. D. Lewis, T. B. Malloy, Jr., T. H. Chao, and J. Laane, J. Mol. Struct. **12**, 427 (1972).
[21] T. Ikeda and R. C. Lord, J. Chem. Phys. **56**, 4450 (1972).
[22] J. R. Durig, Y. S. Li, and L. A. Carreira, J. Chem. Phys. **58**, 2393 (1973).
[23] R. Davidson and P. A. Warsop, J. C. S. Faraday Trans. II **68**, 1875 (1972).
[24] D. W. Wertz, J. Chem. Phys. **51**, 2133 (1969).
[25] L. Pierce and M. Hayashi, J. Chem. Phys. **35**, 479 (1961).
[26] U. Blukis, P. H. Kasai, and R. J. Myers, J. Chem. Phys. **38**, 2753 (1963).
[27] I. Wang, C. O. Britt, and J. E. Boggs, J. Amer. Chem. Soc. **87**, 4950L (1965), and J. L. Alonso (unpublished data).