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The Non-planarity of the Ring Atoms in 2-Oxotetrahydrothiophen

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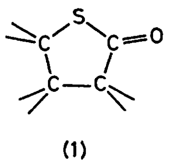
Summary The microwave spectrum of 2-oxotetrahydrothiophen has been studied in the ground vibrational state and is interpreted in terms of non-planarity of the heavy atom skeleton.

In five-membered rings competing forces of strain in valence angles and torsional forces around the C–C bonds of the ring determine which conformation the ring assumes. The ring strain would tend to make the ring planar while the torsional forces would tend to twist or bend the ring. Previous microwave studies of saturated five-membered ring molecules[1] have shown them to have a non-planar arrangement of the heavy atoms. In these molecules, adjacent methylene protons tend to reach a staggered configuration by puckering the skeletal ring to minimize the torsional forces between these groups.

In order to determine the planarity or non-planarity of the heavy atom skeleton of 2-oxotetrahydrothiophen (**1**), we recorded its microwave spectrum which consists of strong a-type and weaker b-type transitions. Measurements were made in the frequency range 18·0—26·5 GHz and low J transitions assigned by Stark effect patterns. c-Type transitions are much weaker in intensity and although some of them were observed, it was possible to measure only one precisely ($3_{1,2} \leftarrow 2_{0,2}$) because of the high density of the spectrum. A rigid rotor analysis of 20 transitions with $J \leqslant 7$ has been made. All measured transitions follow the rigid rotor behaviour and their assignments and observed frequencies are listed in Table 1, together with the differences between observed and calculated frequencies derived from rotational constants given in Table 2.



(1)

Table 1. Rotational transition frequencies (in MHz) of 2-oxo tetrahydrothiophen.

Transitions	ν(obs)	$\Delta\nu^{a}$
$3_{1,2} \leftarrow 2_{0,2}$	20845·93^{b}	−0·22
$3_{2,2} \leftarrow 2_{1,1}$	19192·02	0·04
$3_{3,0} \leftarrow 2_{2,1}$	25232·95	0·17
$4_{2,3} \leftarrow 3_{1,2}$	22505·13	−0·16
$4_{2,2} \leftarrow 3_{2,1}$	22858·80	0·06
$4_{2,3} \leftarrow 3_{2,2}$	19937·97	0·07
$4_{3,1} \leftarrow 3_{3,0}$	21923·03	−0·01
$4_{3,2} \leftarrow 3_{3,1}$	21099·37	0·15
$5_{0,5} \leftarrow 4_{0,4}$	21243·54	0·05
$5_{1,5} \leftarrow 4_{0,4}$	21260·17	0·02
$5_{1,4} \leftarrow 4_{1,3}$	25102·75	−0·05
$5_{2,4} \leftarrow 4_{1,3}$	25614·23	0·02
$5_{1,5} \leftarrow 4_{1,4}$	21195·65	−0·04
$5_{0,5} \leftarrow 4_{1,4}$	21178·85	−0·17
$5_{2,4} \leftarrow 4_{2,3}$	24310·11	0·02
$5_{3,3} \leftarrow 4_{3,2}$	26198·79	−0·06
$6_{0,6} \leftarrow 5_{0,5}$	25120·69	−0·03
$6_{1,6} \leftarrow 5_{1,5}$	25108·12	0·03
$6_{2,5} \leftarrow 6_{0,6}$	18721·15	0·12
$7_{3,5} \leftarrow 7_{1,6}$	18486·79	−0·09
$7_{1,6} \leftarrow 7_{1,7}$	22097·87	−0·13

[a] $\Delta\nu = \nu(\text{obs}) - \nu(\text{calc})$ and ν(calc) is obtained from the rotational constants listed in Table 2. [b] Not used to calculate the rotational constants.

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

A	4448·763 ± 0·012
B	3143·284 ± 0·006
C	1948·563 ± 0·003
I_a	113·59922 ± 0·00032
I_b	160·77963 ± 0·00030
I_c	259·35834 ± 0·00039
$\frac{1}{2}(I_c - I_a - I_b)$	−7·51026 ± 0·00043

[a] Conversion factor: $I_a = 5{\cdot}05376 \times 10^5/\text{Å}$, corresponding to $^{12}C = 12$ atomic-weight scale.

A test for strict planarity comes from the measured moments of inertia, since the out-of-plane contributions to the moments (if zero-point vibrational effects are neglected), $\frac{1}{2}(I_c - I_a - I_b)$, can be calculated from equation (1) where

$$\tfrac{1}{2}(I_c - I_a - I_b) = -\Sigma_i m_i c_i^2$$

m_i is the mass of the ith atom, c_i is the out-of-plane distance, and the I-values are the three moments of inertia. The observed out-of-plane contribution is too large to arise from the hydrogen atoms only. If a C–H bond length of 1·096 Å and a tetrahedral angle of 109° 28′ are assumed for the methylene group parameters, $\frac{1}{2}(I_c - I_a - I_b)$ can be calculated to be −4·843 a.m.u. Å^2. The value of −7·510 a.m.u. Å^2 measured for (**1**) must contain an appreciable contribution from the heavier atoms. The large difference between calculated and observed values can only be explained on the basis of a non-planar ring configuration.

A second test for planarity comes from the potential function of ring puckering modes. If the molecule is planar or near-planar and the potential function for the ring-puckering vibration has a double minimum with a low barrier at the planar configuration, tunnelling through the barrier causes the vibrational levels to be split with a consequent doubling of the observed lines in the spectrum. If the barrier is high enough, the molecule is permanently puckered and the c dipole component is not zero. Here, no splitting of the levels is observed and c-type transitions are observed so that the skeletal ring of (**1**) is non-planar.

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[1] H. Kim and W. D. Gwinn, *J. Chem. Phys.*, 1969, **51**, 1815; G. G. Engerholm, A. C. Luntz, W. D. Gwinn, and D. O. Harris, *ibid.*, **50**, 2446; A. C. Legon, *Chem. Commun.*, 1970, 838; J. R. Durig, Y. S. Li, and C. C. Tong, *J. Mol. Struct.*, 1973, **18**, 269; I. Wang, C. O. Britt, and J. E. Boggs, *J. Am. Chem. Soc.*, 1965, **87**, 4950; P. A. Baron and D. O. Harris, *J. Mol. Spectrosc.*, 1974, **49**, 70; R. C. Loyd, S. N. Mathur, and M. D. Harmony, *ibid.*, 1978, **72**, 359; J. Choe and M. D. Harmony, *ibid.*, 1980, **81**, 480; J. L. Alonso, *J. Mol. Struct.*, 1981, **73**, 71.