

Number 2  
1982

## Microwave Spectrum and Double Minimum Potential for the Ring Puckering Vibration of 2,5-Dihydrothiophen *S,S*-Dioxide

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The microwave spectra of the ground and five excited states of the ring puckering vibration of 2,5-dihydrothiophen *S,S*-dioxide show this vibration to have a double minimum potential function with a barrier of *ca.* 100 cm<sup>-1</sup> to planarity of the ring.

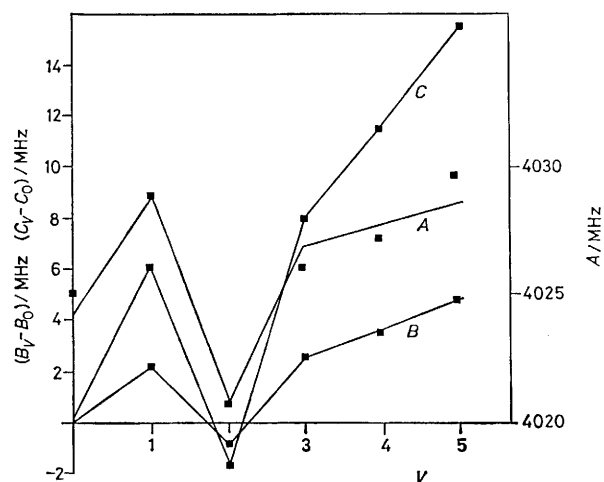
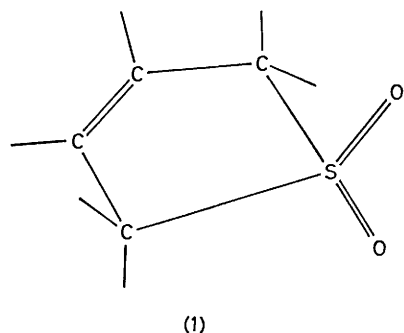
An *X*-ray crystal structure determination showed the 2,5-dihydrothiophen *S,S*-dioxide (**1**) to have *C*<sub>2v</sub> symmetry.<sup>1</sup> We have observed the microwave spectrum of the ground and first five excited states of the ring puckering vibration of this molecule and believe these data show that the vibration has a double minimum potential function.

Microwave spectra in the frequency range 18–40 GHz were observed at room temperature using a Hewlett-Packard 8460A microwave spectrometer at Harvard University with a sample of the sulphone (**1**) (99% pure) supplied by Aldrich. Because of the low volatility (*m.p. ca.* 338 K) of (**1**) prolonged conditioning of the cell was required in order for the microwave spectrum to be observed.

The *X*-ray structure predicts the sulphone (**1**) to be a prolate asymmetric rotor with Ray's asymmetry parameter  $\kappa$  *ca.* -0.9, *B* + *C ca.* 4030 MHz and to have  $\mu_a$  dipole selection rules. Low-resolution microwave spectra showed a series of  $\mu_a$  *R*-branch bands with *B* + *C* = 4187 ± 5 MHz.

The most prominent feature of the high-resolution microwave spectrum is the presence of two series of  $\mu_a$  *R*-branch lines which are indistinguishable in intensity when allowance

is made for the 9:7 statistical weight effects of three pairs of hydrogen atoms. The most obvious interpretation of this doubling of the microwave spectrum is for the ring puckering vibration to have a double minimum potential function as in trimethylene sulphide<sup>2</sup> and  $\Delta^1$ -pyrazoline<sup>3</sup> and for the two series of lines to be due to the ground (*V* = 0) and first excited (*V* = 1) states of this vibration. Higher excited states of this vibration up to *V* = 5 were readily assigned on the basis of relative intensities and statistical weight effects. The line frequencies of the *V* = 2 and higher states were found to fit semi-rigid rotor theory within the experimental error of the measurements (*ca.* 0.1–0.2 MHz) using only a single centrifugal distortion constant  $\Delta_{JK}$ . The line frequencies of the *V* = 0 and *V* = 1 states show considerable deviations from semi-rigid rotor theory; the discrepancies increased with the



**Figure 1.** Variation of rotational constants with vibrational quantum number (*v*) for the sulphone (**1**). Points represent observed values and solid lines represent the values calculated for the potential  $V(X) = v_0(X^4 - \eta X^2)$  with  $\eta = 6.5$ .

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**Table 1.** Rotational constants for the sulphone (1)<sup>a</sup>

<i>V</i>	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	$\Delta_c/(10^4 \text{ M}_u \text{ pm}^2)$
0	4025.2	2156.215	2000.102	107.3
1	4028.9	2158.435	2006.292	107.7
2	4020.6	2155.420	1998.314	107.3
3	4026.1	2158.739	2008.223	108.0
4	4027.2	2159.770	2011.697	108.3
5	4029.7	2161.021	2015.773	108.6

<sup>a</sup> Standard errors are approximately 1 MHz on *A*, and 0.01 MHz on *B* and *C* for all vibrational states.

$K_{-1}$  pseudo-quantum number and reached *ca.* 250 MHz for the  $9_{6,4} \leftarrow 8_{6,3}$  and  $9_{6,3} \leftarrow 8_{6,2}$  transitions of both states. Considering the size of these deviations a satisfactory fit to both states together was obtained using the reduced axis system Hamiltonian of Pickett<sup>5</sup> with an *Fac* coupling term and an energy separation  $E_{0-1}$  of  $1.64 \text{ cm}^{-1}$ . Relative intensity measurements<sup>4</sup> gave the following energy separations  $E_{1-2}$  *ca.*  $70 \text{ cm}^{-1}$  and  $E_{2-3}$  *ca.*  $35 \text{ cm}^{-1}$ . Table 1 gives preliminary rotational constants and values of  $\Delta_c = I_a + I_b - I_c$  and Figure 1 shows the variation of rotational constants with vibrational quantum number.

The simple potential function  $V(X) = \nu_0(X^4 - \eta X^2)$ , where *X* is a reduced co-ordinate,<sup>6</sup> has been used to estimate the barrier to ring planarity using the observed energy separations and also the variation of the rotational constants with vibrational quantum number.<sup>2,3</sup> The energy separations indicate  $\eta = 8.5$  and, using  $E_{1-2} = 70 \text{ cm}^{-1}$  to determine  $\nu_0$ , a barrier height of  $120 \text{ cm}^{-1}$ . Fitting the vibrational constants to express-

$$B = \beta_0 + \beta_2 \langle X^2 \rangle + \beta_4 \langle X^4 \rangle \quad (1)$$

ions of the form<sup>2,3</sup> of equation (1) gives a lower value of  $\eta = 6.5$  and, using the same energy separation to determine  $\nu_0$ , a barrier of  $90 \text{ cm}^{-1}$ .

Evidence for the non-planarity of the ring comes from  $\Delta_c$ . Hargittai<sup>7</sup> has recently shown that in a number of  $\text{XSO}_2$  sulphones with  $C_{2v}$  symmetry the oxygen atoms contribute  $(98.8 \pm 0.6) \times 10^4 \text{ M}_u \text{ pm}^2$  to  $\Delta_c$ . Assuming  $r(\text{H} \dots \text{H}) = 185 \text{ pm}$  for the methylene hydrogens<sup>7</sup> a value of  $\Delta_c = (105.7 \pm 0.6) \times 10^4 \text{ M}_u \text{ pm}^2$  is predicted for the sulphone (1) with  $C_{2v}$  symmetry. The observed ground-state value is somewhat larger than this. The value of  $\Delta_c$  calculated from the  $\beta_0$  values of equation (1) which correspond to a  $C_{2v}$  symmetry structure<sup>3</sup> is  $105.8 \times 10^4 \text{ M}_u \text{ pm}^2$ , in good agreement with the value predicted from Hargittai's work.

One of us (J. L. A.) thanks Professor E. B. Wilson and members of his research group for helpful discussions. We thank Dr. I. Hargittai for sending us a preprint of his work.

Received, 5th October 1981; Com. 1165

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