The Generation and Microwave Spectrum of Propadienethione, $H_2C{=}C{=}C{=}S$

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The third member of the cumulenethione series, H_2C_nS, propadienethione, has been produced by pyrolysis of cyclopenteno-1,2,3-thiadiazole and detected by microwave spectroscopy which provided rotational parameters for the ^{32}S and ^{34}S isotopomers, the dipole moment [2.064(8) Debye], and an indication that propadienethione is a planar molecule of C_{2v} symmetry.

The cumulenone series of compounds, H_2C_nO, was until recently[1,2] not known beyond the second member. It is of special interest because, in contradiction to the theory of cumulated double bonds going back to van't Hoff,[3] the third member, propadienone, has been shown to be kinked at the central carbon atom.[4—6] However valence theory, which predicted the subsequent members of the series to be even more kinked,[7] has been shown to be in error for the fourth member of the series, butatrienone.[8] It is clearly of interest to ascertain whether such peculiarities occur in related series such as the cumulenethiones, a series in which again only the first two members have been hitherto fully characterized. We report here the characterization of the third member of this series, propadienethione, by microwave spectroscopy.

The compound was generated by pyrolysis of cyclopenteno-1,2,3-thiadiazole (**1**) which was expected to fragment to N_2, ethylene, and propadienethione as shown in Scheme 1.

We had considered an alternative pyrolytic pathway through an anthracene derivative, but this has the disadvantage of being a solid and of possibly generating relatively involatile anthracene as one of the pyrolysis products. Very recently it has been reported that pyrolysis of this anthracene derivative does indeed yield propadienethione although the identification rests only upon assignment of two i.r. frequencies.[9]

Table 1. Rotational (*A*,*B*,*C*) and centrifugal distortion (*D*,*H*) constants for propadienethione.

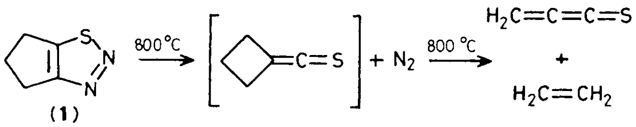
Parameter/MHz	$H_2C_3{}^{32}S$	$H_2C_3{}^{34}S$
A	328500 (26700)	328500[a]
B	2539.276 (1)[b]	2476.927 (5)
C	2515.681 (1)	2454.456 (5)
D_J	0.000162 (5)	0.000143 (40)
D_{JK}	0.0654 (4)	0.0627 (19)
H_{KJ}	−0.00157 (5)	−0.00152 (20)

[a] Parameter held at main species value.

[b] Numbers in parentheses are one standard deviation from the least squares fit, expressed in terms of the last digit.

The precursor (**1**) was pyrolysed at 800 °C in a short quartz oven close to a 1.5 metre long *G*-band (4.76 × 2.22 cm) waveguide cell fitted with a septum for Stark modulation. A search between 26.5 and 40.0 GHz rapidly revealed two groups of microwave absorption lines with patterns identical to those expected for a near prolate symmetric top molecule, and at frequencies very close to those predicted for H_2C_3S from a geometry optimized at the DZ + P level of theory.[10] The spectrum was readily assigned from observation of Stark effects and a least squares fit of 18 *R*-branch transitions for $J'' = 4$—11 between 25 and 61 GHz led to the spectroscopic constants listed in Table 1. Absorption lines of even and odd K_{-1} values show a 1 : 3 intensity alternation indicating the presence of two equivalent protons and hence C_{2v} symmetry about the *a*-axis.

Further confirmation comes from the observation and assignment of weak sets of lines, (of the expected relative intensity) at frequencies below those of the main species, to $H_2C_3{}^{34}S$. The spectroscopic constants from a fit of 10 *R*-branch transitions are included in Table 1. The only plausible identification of the compound is seen to be propadienethione. The dipole moment, obtained by analysis of the Stark effect of the 5_{05}—4_{04} and 5_{15}—4_{14} transitions is 2.064(8) Debye, about the expected value for the thione when



Scheme 1

the trends in dipole moments of the two cumulene series are examined.

The inertial defect, 0.328 $m_{\mu}Å^2$, is consistent with the molecule being planar but the large uncertainty in the *A* rotational constant precludes any definite statement. In our experience the uncertainties in the constants derived from least squares fits of the type employed in this study are greater than the calculated standard deviations, owing to model inadequacies. The evidence for propadienethione being a planar molecule with a linear heavy atom skeleton is strong, but owing to our past experience with the kinked molecule propadienone we cannot definitely assign the geometry of propadienethione until we obtain spectra for some other rare isotopomers.

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