Microwave Spectrum, Structure, and Dipole Moment of 4*H*-Thiapyran-4-thione

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Summary In a search for the microwave spectrum of 1,6,6a-trithia(6a-S^{IV})pentalene a weak spectrum was detected and assigned to small quantities of 4*H*-thiapyran-4-thione whose structure and dipole moment were subsequently determined using a prepared sample.

The present study was prompted by the current controversy concerning the structure of trithiapentalene ring systems. Investigations of the unsubstituted parent compound by *X*-ray crystallography,[1] electron diffraction,[2] and ESCA[3] were best interpreted in terms of a C_{2v} symmetrical structure with equal sulphur–sulphur bonds, but the question still remains whether the central sulphur atom lies in a single or double potential minimum.† We hoped to settle this question *via* the microwave spectrum but extensive searches failed to detect assignable lines, despite the use of a wide range of experimental conditions over a period of many weeks. However, a weak spectrum, not attributable to trithiapentalene, did develop; it clearly belonged to a near-prolate asymmetric rotor (κ *ca.* $-0{\cdot}90$) with characteristic μ_a, *R*-branch patterns occurring as $J = 12 \rightarrow 13$ through $J = 16 \rightarrow 17$ in the 26—40 GHz region. Trithiapentalene was expected to have a more complicated μ_b spectrum with the additional possibility of a spectrum associated with an inverting μ_a dipole. The observed spacings were inappropriate for either of these possibilities for trithiapentalene. The moments of inertia derived from a preliminary analysis plus evidence of nuclear spin weightings suggested a C_{2v}, planar ring compound, most probably 4*H*-thiapyran-4-thione, a new microwave species. A literature search showed that the chemistry of the two systems was interrelated[4] and that trithiapentalene and thiapyranthione

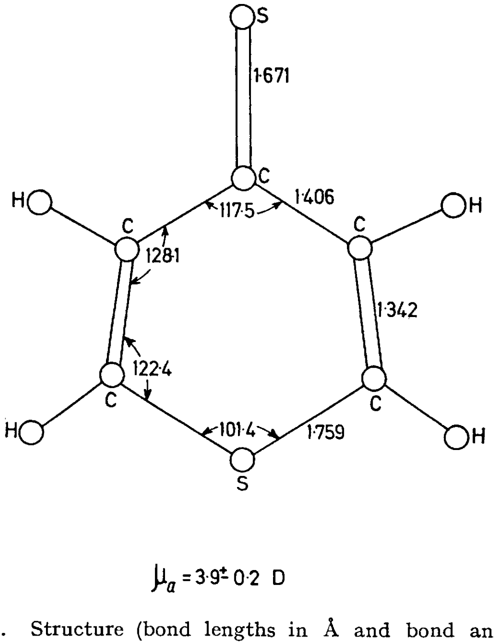

Figure. Structure (bond lengths in Å and bond angles in degrees) and dipole moment of 4*H*-thiapyran-4-thione.

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† Theoretical calculations are summarised in reference 3.

might be interconvertible.[5] In the present work the conversion took place after the trithiapentalene sample had been at temperatures up to 60 °C in a copper waveguide for several days, and probably involved loss of sulphur at the metal surface. (A similar conversion, possibly metal catalysed, has recently been reported[6] in a mass spectral study using high ion source temperatures). The sample was removed from the cell for mass spectral analysis which showed it to contain a few percent of thiapyranthione in mainly trithiapentalene, thus confirming the microwave identification. Conclusive proof was obtained by preparing 4*H*-thiapyran-4-thione by a recognised method[4] and matching its intense microwave spectrum with the impurity pattern previously obtained.

TABLE. Rotational constants (MHz) and inertial defect (a.m.u.Å^2) of 4*H*-thiapyran-4-thione.

A	5 078·1 ± 0·2
B	1 180·288 ± 0·005
C	957·892 ± 0·005
10^3D_J	0·017 ± 0·008
10^3D_{JK}	0·050 ± 0·009
$I_c - I_a - I_b$	−0·110 ± 0·005

The ground-state rotational constants of 4*H*-thiapyran-4-thione, obtained from a least-squares fit to the observed frequencies, are given in the Table. Small centrifugal distortion effects were taken into account using a symmetric-top approximation. The small value of the inertial defect is indicative of a planar molecule and the C_{2v} symmetry is confirmed from the 10:6 alternation of intensity with even and odd K_{-1} in the ground-state spectrum. A vibrational satellite series has also been observed up to the third excited state and this too shows clearly the effects of nuclear spin statistics. This lowest vibrational mode is estimated from relative intensity measurements to be at 100 ± 20 cm^{-1}, and the intensity alternations require it to be a perpendicular mode (B_1 or B_2 species of the C_{2v} point group).

Isotopic substitution data have been obtained from the spectra of the following species in natural abundance: the two ^{34}S species (4%) and one ^{13}C species (1%) on the symmetry axis, and the ^{13}C species (2%) adjacent to the in-ring sulphur position. These data have been used to derive an accurate structure for the heavy-atom skeleton of 4*H*-thiapyran-4-thione (Figure). Its dipole moment has also been measured as 3·9 ± 0·2 D‡ using a new application[7] of the first-order Stark effect suitable for high J transitions.

4*H*-Thiapyran-4-thione forms the fourth member of an oxygen–sulphur series 4*H*-pyran-4-one, 4*H*-pyran-4-thione, and 4*H*-thiapyran-4-one, all of which have now been studied by microwave spectoscopy.[8] Interest in this series derives from the question of aromaticity,[9] whether this be argued from the standpoint of chemical reactivity[10] or from physical measurements such as ring currents[11] or magnetic susceptibility anisotropies.[12] The microwave spectra, structures, and dipole moments of these analogues will be presented in a forthcoming paper[13] in which that question will be discussed.

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‡ 1 D = 10^{-18} e.s.u. cm = 3·335 × 10^{-30} C m.

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