Ethenethiol: an Infared and Microwave Spectroscopic Study

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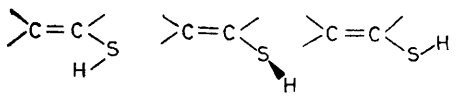
Summary Microwave and i.r. spectra of ethenethiol have been obtained and the predominant conformation of the molecule shown to be planar or near-planar *s-cis*.

ETHENETHIOL is a molecule of considerable spectroscopic and theoretical interest. Until relatively recently the molecule was considered to be unstable. Although in 1965 Strausz *et al.* published a well documented account of its synthesis,[1] the question of the preferred molecular conformation has been an open one. There are three main possibilities: *s-cis* or *syn* (**1**), non-planar or *gauche* (**2**), and *s-trans* or *anti* (**3**).



(1) (2) (3)

We have used essentially the same method of preparation as in ref. 1 (irradiating a mixture of acetylene and hydrogen sulphide with u.v. light), but have carried out the whole reaction in the gas phase at pressures less than atmospheric thus minimizing the obvious risks of explosions. Details of the experimental arrangement will be published elsewhere.

A partial purification of the irradiation products was effected by distillation under reduced pressure, and the resulting ethenethiol was transferred to an i.r. cell, a microwave cell, or sprayed on to a cooled window of a cryostat. Spectral analysis of the product showed that considerable decomposition occurs after a few hours and we found that the compound has an approximate half life at ambient temperatures ranging from 1 h to several days depending on the material of the vessel in which it is contained.

The i.r. spectrum shows a very strong absorption at 1603 cm^{-1} corresponding to the C=C stretching mode, and several other bands with well resolved rotational contours are clearly seen. Strong type C contours, arising from out-of-plane vibrations of the vinylic hydrogens and indicative of a planar molecular framework are seen at 957 and 872 cm^{-1}, both having characteristic *Q* branch fine structure on the *P* and *R* envelopes. An analysis of these *Q* band structures showed the mean splitting to be 2·94 ± 0·05 cm^{-1}. For a prolate-top molecule, the separation is given by $2\ [A - \{(B + C)/2\}]$. Evaluating this quantity for the two planar models of ethenethiol gives *s-cis* 2·89 and *s-trans* 3·14 cm^{-1}. The following structural parameters were used for the model: C=C, 133·0 pm; C–H, 109·0 pm; C–S, 177·6 pm; and S–H, 134·0 pm; ∠H–C–H 120; ∠C=C–S 126; and ∠C–S–H 97°. Clearly the most likely conformation for the molecule is planar *s-cis*.

TABLE. Rotational constants/MHz.

	Observed	Planar *cis*	Planar *trans*
A	49890 ± 600	48831·00	52464·63
B	5835·67 ± 0·27	5837·58	5702·37
C	5222·16 ± 0·32	5214·23	5143·34

We have also carried out matrix isolation i.r. experiments using Ar and N_2 matrices at 15 K, and our results, together with data from i.r. spectra of the vapour phase and from microwave spectra enable us to feel confident that all fifteen normal modes can be assigned to selected absorptions.

Analysis of the microwave spectrum of ethenethiol confirms the conclusions drawn from the i.r. spectra and provides stronger evidence that the preferred conformation is *s-cis*. Amongst the most intense absorptions in the observed spectrum are sets of low $J\ \mu_a$ *R*-branch transitions, and the associated rotational constants are shown in the Table. No μ_b transitions have been assigned to date so the poorly determined *A* rotational constant precludes the use of the inertial defect to establish the planarity of the species. However, it can be seen that the constants (Table) are very close indeed to those predicted for the planar *s-cis* form of the molecule using the model parameters quoted above. Further evidence in support of this conclusion cames from simple bond moment calculations of the dipole moment components along the molecular principle axes. These show that only the planar *s-cis* form of the molecule is expected to have a μ_a dominated spectrum. Preliminary values for the dipole components have been obtained from measurements of the Stark effects of the $J = 1 \rightarrow 2\ \mu_a$ transitions as, $\mu_a = 0{\cdot}82 \pm 0{\cdot}05$ and $\mu_b = 0{\cdot}40 \pm 0{\cdot}30$ D, assuming $\mu_c = 0{\cdot}0$.

Several vibrational satellites accompanying each ground state line have been assigned and are currently being analysed. Our data show convincingly that ethenethiol exists predominately in a planar or near-planar *cis* conformation, and we are currently searching for evidence of another conformation using both microwave and i.r. spectroscopy.

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[1] O. P. Strausz, T. Hikida, and H. E. Gunning, *Canad. J. Chem.*, 1965, **43**, 717.