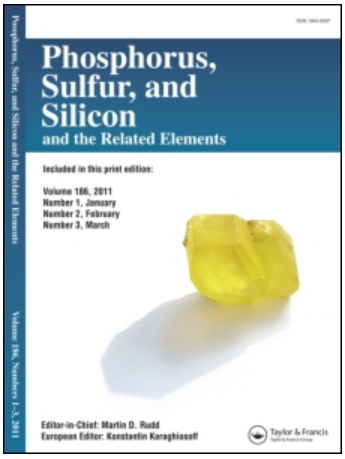

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INTRAMOLECULAR OH···S HYDROGEN BONDS AND MOLECULAR CONFORMATIONS IN 2-METHYLMERCAPTOETHANOL

Peter J. Krueger[a]; Ronald A. Kydd[a]; Surjit Singh[b]
[a] Department of Chemistry, University of Calgary, Calgary, Canada [b] Department of Chemistry, Indian Institute of Technology, Madras, India

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INTRAMOLECULAR OH•••S HYDROGEN BONDS AND MOLECULAR CONFORMATIONS IN 2-METHYLMERCAPTOETHANOL

Peter J. Krueger, Ronald A. Kydd and Surjit Singh*
Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4 (*C.I.D.A./N.R.C. Research Associate. Permanent Address: Department of Chemistry, Indian Institute of Technology, Madras 600036, India).

The infrared absorption spectrum of monomeric 2-methylmercaptoethanol in dilute CCl_4 solution exhibits four overlapped bands in the fundamental OH stretching region. The individual band components were resolved using digital computing techniques [1], and the relative band intensities are temperature dependent. The "free" OH bands at 3634 and 3623 cm^{-1} correspond to gauche and trans orientations about the C-O bond, respectively, by analogy with similar band components in the infrared spectrum of ethanol in dilute CCl_4 solution. The OH bands at 3539 and 3446 cm^{-1} are assigned to gGt and gGg' conformers, respectively, each involving an intramolecular OH•••S hydrogen bond (conformer notation refers to the orientation about the C-O, C-C and C-S(CH_3) bonds, respectively). A similar interpretation of the matrix isolated infrared spectra of ethylene glycol, involving two conformers with intramolecular OH•••O hydrogen bonds and differing principally in the orientation of the proton-acceptor OH group, has been presented recently [2]. The microwave spectrum of 2-mercaptoethanol in the vapour phase arises from an all-gauche conformation with an intramolecular OH•••S hydrogen bond [3].

The relative stability of conformers giving rise to the bands observed for 2-methylmercaptoethanol were established to be as follows in this study:

"free" OH(trans) > gGt(OH•••S) > "free" OH(gauche) >> gGg'(OH•••S)

ΔH(kcal/mole)	0	1.1	2.9	<<3

The conformer with the largest OH frequency shift (177 cm^{-1}), and presumably with the strongest intramolecular OH•••S hydrogen bond, is the least stable of all the conformers observed. Steric hindrance must be a major factor destabilizing this conformer. Substitution of alkyl groups larger than methyl on sulfur lead to the complete absence of this low frequency OH band at room temperature, while the other three components remain.

Raman spectra of 2-methylmercaptoethanol in various solvents and over a temperature range suggest that the C-S stretching vibrations are not shifted significantly by intramolecular OH•••S hydrogen bonding. However, the trans

orientation about the C-S bond is more stable than the gauche orientation, in contrast to what is observed in ethyl methyl sulfide [4].

These spectral observations are discussed in relation to conformational mobility in ethyl alcohol, ethyl methyl sulfide and ethylene glycol. A highly significant feature of this study is the demonstration that trans/gauche re-orientation of an electronegative proton-acceptor group involved in an intramolecular hydrogen bond can induce substantial changes in the character of the intramolecular OH•••X hydrogen bond.

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