

THE SPECTRA AND STRUCTURES OF SULPHUR-CONTAINING COMPOUNDS

Part III. The vibrational spectra and conformations of acyclic sulphoxides*

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ABSTRACT

The IR and Raman spectra of the acyclic sulphoxides $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{Cl}$, $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{Br}$, *p*- $\text{ClC}_6\text{H}_4\text{S}(\text{O})\text{CH}_2\text{Cl}$ and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{S}(\text{O})\text{CH}_2\text{Br}$ in their liquid and crystalline states and IR solution spectra have been recorded. A normal coordinate analysis has been carried out, an interpretation of the vibrational spectra given and the force fields determined. It has been shown that acyclic sulphoxides exist as a mixture of conformations in the liquid and in solutions. The values of ΔH for the relative stabilities have been determined from the IR spectra of solutions at different temperatures.

INTRODUCTION

In recent years social studies have been made of internal rotation about S—C, S—O and S—N bonds by vibrational spectroscopic methods. On the whole, however, the vibrational spectra and stereochemistries of the acyclic sulphoxides have been little investigated. The vibrational spectra of dimethylsulphoxide were reported by Forel and Traquilie [1] while the IR and Raman spectra of some $\text{XC}_6\text{H}_4\text{S}(\text{O})\text{CH}_3$ species were measured and a vibrational assignment undertaken by Kresze et al. [2]. The $\nu(\text{S}=\text{O})$ absorption in the IR spectra of some simple dialkyl sulphoxides has also been studied [3]. The doublets observed in this region were stated to be due to rotational isomers, however, similar results [4] have been discussed on the basis of Fermi resonance and solvent effects.

This paper reports an investigation of the vibrational spectra and conformations of the acyclic sulphoxides $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{Cl}$ (I), $\text{CH}_3\text{S}(\text{O})\text{CH}_2\text{Br}$ (II), *p*- $\text{ClC}_6\text{H}_4\text{S}(\text{O})\text{CH}_2\text{Cl}$ (III) and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{S}(\text{O})\text{CH}_2\text{Br}$ (IV). An electron diffraction study of dimethyl sulphoxide [5] suggests that three non-equivalent conformations resulting from rotation about the S— CH_2X bond are possible for the sulphoxides I–IV (Fig. 1).

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