The spectra and structure of sulphur-containing organic compounds—V. The vibrational spectra and conformations of \( p\-\text{RC}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{X} \) sulphones

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Abstract—The i.r. and Raman spectra of \( p\-\text{RC}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{X} \) (\( R = \text{H}, \text{CH}_{3}, \text{Cl}, \text{Br}; X = \text{Cl}, \text{Br} \)) sulphone liquid solutions and crystals have been investigated. The existence of a mixture of trans and gauche conformations in liquid and solution phases has been established. The temperature dependences of the i.r. spectra have been studied and the values of \( \Delta H = H(\text{gauche}) - H(\text{trans}) \) determined. The molecular conformations in the crystal have been determined by the dichroism of polarized i.r. spectral bands. In the case of \( \text{CH}_{3}\text{C}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{Br} \) polymorphic crystal modifications, differing in molecular conformations, have been found. An interpretation of the vibrational spectra is given.

**INTRODUCTION**

CH\( _3\)SO\( _2\)CH\( _2\)X sulphones in liquid and solution phases are in both trans and gauche conformations [1]. The energy values of the conformations are close and \( \Delta H \approx 0 \). It is interesting to investigate the effect of the replacement of the CH\( _3 \) group by \( p\-\text{RC}_{6}\text{H}_{4} \). The conformations of \( p\-\text{RC}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{X} \) sulphones have been studied only by dipole moment and Kerr's constant methods [2, 3]. It is concluded in Ref. [2] that in a benzene solution the sulphones are in the gauche conformation. In the opinion of the authors of Ref. [2] this confirms a new conformation rule, according to which a symmetric arrangement of the polar bonds is disadvantageous. However, it was concluded in [3] that the \( p\-\text{RC}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{X} \) sulphones in solution are in the form of a mixture of trans and gauche conformations. Unfortunately, the results of conformational analysis by dipole moment and Kerr's constant methods are materially affected by the choice of parameters. A comparison of Refs [2] and [3] shows that the values of the parameters and their selection are not unambiguous. In this paper an investigation of the vibrational spectra and of the conformations of \( p\-\text{RC}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{Cl} \) \( R = \text{H} \) (I), \( \text{CH}_{3} \) (II), Cl (III), Br (IV); \( p\-\text{RC}_{6}\text{H}_{4}\text{SO}_{2}\text{CH}_{2}\text{Br} \) \( R = \text{H} \) (V), \( \text{CH}_{3} \) (VI), Cl (VII), Br (VIII) sulphones has been carried out.

**EXPERIMENTAL**

The i.r. spectra in the 400–4000 cm\(^{-1}\) range were measured with a Karl Zeiss UR-20 spectrometer. The Raman spectra were recorded by a DFS-24 He-Ne laser spectrometer. The experimental procedure was similar to that described in [4, 5]. Sulphone I–VIII synthesis is described in [3].

**RESULTS AND DISCUSSION**

It can be assumed that, as in the case of haloid-methylsulphone [1], two inequivalent conformations of sulphones I–VIII are possible with trans and gauche orientations of the C–X and S–C bonds. The number of conformations in liquid and solution phase was determined by comparing the liquid and crystal spectra. Crystalization of sulphones I–VIII is accompanied by the disappearance (freezing out) of the following bands in the i.r. spectra and lines in the Raman spectra (Tables 1–4): sulphone I, the 517, 585, 708, 723 cm\(^{-1}\) bands and the 515 and 711 cm\(^{-1}\) lines; sulphone II, the 662 cm\(^{-1}\) bands and the 213 cm\(^{-1}\) line; sulphone III, the 463, 546, 568, 1126 cm\(^{-1}\) bands and the 223, 287, 463, 544, 666, 702, 798 and 1127 cm\(^{-1}\) lines; sulphone IV, the 541 cm\(^{-1}\) band and the 161, 311 and 538 cm\(^{-1}\) lines; sulphone V, the 512 and 712 cm\(^{-1}\) bands and the 495 cm\(^{-1}\) line; sulphone VI, the 463, 541 and 564 cm\(^{-1}\) bands and the 207, 279, 306, 370, 458, 541 and 564 cm\(^{-1}\) lines; sulphone VII, the 541 cm\(^{-1}\) band. When the liquid sulphone VI film between KBr plates is rapidly or slowly cooled, two crystalline modifications are obtained (crystal I and crystal II), which differ significantly in their i.r. spectra (Table 2, Fig. 1). In the crystal I spectra the 638 and 1199 cm\(^{-1}\) bands are frozen out, while in the crystal II spectra this happens to the 626 and 1212 cm\(^{-1}\) bands and the 628 cm\(^{-1}\) line. In addition, some bands in the crystal I and II spectra differ in relative intensity and position in the spectrum. For example, the 464 and 516 cm\(^{-1}\) bands are observed in the i.r. spectrum of liquid sulphone VI, 461 and 520 cm\(^{-1}\) bands correspond to them in the crystal I spectrum, and the 478 and 507 cm\(^{-1}\) bands in the crystal II spectrum (Table 2).

These experimental data on the vibrational spectra of sulphones I–VIII may be explained only by the presence of a mixture of trans and gauche conformations in liquid sulphones. Only one of them remains