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The Infrared Spectra of Pressed-disc Samples in Relation to Molecular Structure in 2,3-Dibromo-2,3-dimethylbutane

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THE majority of derivatives of ethane are liquids at room temperature. The molecular structure of those molecules that can exist as rotational isomers can be established from infrared and Raman studies in the liquid and solid phase.[1,2] 2,3-Dibromo-2,3-dimethylbutane is an unusual molecule in this category in that it is a crystalline solid subliming at 159° c. The infrared spectrum of this compound has been measured in order to clarify discrepancies between earlier spectroscopic and dipole-moment work.[3,4] We also report evidence of internal rotation in the solid that occurs during the preparation of pressed-disc samples.

The present infra-red spectra of the solid in mull and crystalline form are similar to the earlier spectra[4] of dilute solutions. When these spectra of the solid are compared with the Raman spectrum[5] of the solid it is clear that the rule of mutual exclusion holds, showing that the molecular form in the crystal is entirely *trans* with molecular symmetry C_{2h}.[6] In the present infrared spectra of the liquid at high temperature, and also of dilute solutions, there are several more absorption bands than in the corresponding spectra of the solid. For example, extra absorption bands appear at 1283, 1263, 1190, 1055, 1020, 1005, 947, 925, 682, and 490 cm.$^{-1}$ This indicates the presence of the *gauche*-isomer in the condensed phase and these extra absorption bands are assigned to the vibrational frequencies of this form. The intensities of these *gauche*-bands are weak and are, therefore, in good qualitative agreement with the energy difference of 1·5 kcal./mole found from the dipole-moment studies.[3] This energy difference indicates that 10—15% of the molecules are in the *gauche*-form and explains why these extra absorption bands were not observed in the earlier spectroscopic measurements.[4] The structure of the molecule is now established, the molecular form being *trans* in the solid, while in the condensed phase the molecule exists as an equilibrium mixture of *trans*- and *gauche*-isomers.

Several more absorption bands were observed in the infrared spectra of the solid in pressed-disc form compared with the spectrum in a mull or in crystalline form. Extra absorption bands appearing in potassium halide pressed-disc spectra have often been reported[7] and these changes have been discussed by Baker[8] who refers to changes in spectra of both first and second order. First-order changes mainly involve intensities and this is clearly evident in absorption bands at 1200 and 1168 cm.$^{-1}$ The second-order changes are more severe with new groups of frequencies appearing which in the present case are the absorption bands at 1282, 1260, 1189, 1016, 1005, 682, and 499 cm.$^{-1}$ respectively. Several factors have been discussed as being responsible for these changes[8] including the crystal energy of the organic phase, the energy of grinding, the matrix lattice energy, the matrix particle size, stress relaxation, and polymorphism.

It is interesting to note that for 2,3-dibromo-2,3-dimethylbutane all the extra absorption bands which appear in the pressed-disc spectra correspond almost exactly in frequency to those absorption bands previously assigned to the *gauche*-isomer. Although not all the *gauche* absorption bands were observed, presumably because they were too weak in intensity or due to the first-order[8] changes mentioned above, we are reasonably certain that these extra absorption bands can be assigned to the *gauche*-isomer.

It is therefore clear that, during the preparation of the pressed-disc samples of the solid, internal rotation has taken place with some molecules going from the *trans*- to the *gauche*-form. This structural change probably takes place during pressing, since the spectrum of the pure pressed-disc sample is similar to those of the potassium halide discs. In preparing a mull sample the solid was ground under similar conditions to the pressed-disc samples.

The energy barriers for the *trans* → *gauche*-transition for similar molecules lie in the range 4—6 kcal./mole,[9] and it is quite feasible that during pressing a polymorphic change in the crystalline structure takes place accompanied by internal rotation in some of the molecules. An analogy to this effect has been observed[10] when supercooling liquid rotational isomers with the formation of a glassy solid. In this form the molecule exists as both *trans*- and *gauche*-forms, but on heating a glassy solid → crystalline solid transition takes place with all the molecules being converted into the more stable form. We believe that this is the first case reported whereby structural changes within the molecule in the form of internal rotation has taken place during the preparation of pressed-disc samples for infrared spectroscopy.

All spectra were recorded with a Hilger 900 Infrascan and a Hilger 800 spectrometer equipped with CsI optics. The pressed discs were prepared using an R.I.I.C. 30-ton hydraulic press. 2,3-Dibromo-2,3-dimethylbutane was a purified sample obtained from K. and K. Ltd.

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