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ROTATIONAL ISOMERS OF PERFLUORO(1-CYCLOHEXYLCYCLOHEXENE)

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During the characterisation of perfluoro(1-cyclohexylcyclohexene)[1] it has been found that the infrared spectrum of this compound displayed two bands, which can be assigned to the valency vibration of the double bond, at 1686 and 1672 cm^{-1} (vapour), the higher-frequency band being the stronger. Since the purity of this olefin had been ascertained by chemical and physical methods,[1] the two double-bond-stretching bands may be thought to arise from the equatorial and axial isomers of this compound. This has been confirmed by measuring the ratio, R, between the intensity of the 1686-cm^{-1} and that of the 1672-cm^{-1} band at -150° (R = 4.24, solid-phase spectrum), +45° (R = 2.84), and +125° (R = 2.21). The downward trend of this ratio indicates that the 1686-cm^{-1} and the 1672-cm^{-1} bands arise from the more stable, equatorial isomer and from the less stable, axial isomer, respectively. This latter, in fact, can be shown to have a much higher degree of steric compression by means of molecular models. The lowering of the double-bond frequency because of steric compression is also shown by another, highly strained, isomeric olefin, perfluoro[4(cyclohexen-1-yl)-1-methylcyclopentane] $\nu_{max.}$ 1670 cm^{-1} (liquid).[1] The energy difference, $\Delta H°$, between the two rotational isomers can be evaluated by the equation

$$A_{ax.}/A_{eq.} = K \exp(-\Delta H°/RT)$$

where $A_{ax.}$ and $A_{eq.}$ are the band absorbances of the axial and of the equatorial isomers, respectively, and are assumed to be proportional to the molecular density, R is the gas constant, and T is the absolute temperature. The ratio $\log(A_{1686\ cm^{-1}}/A_{1672\ cm^{-1}})$ [$A = \log(I_o/I)$] has been measured from vapour-phase spectra at temperatures in the range between +48° and +140° and its values are plotted against 1/T in fig. 1. From the slope of the straight line that can thus be drawn, the energy difference can be worked out to be $\Delta H° = 1013$ cal/mole. The value of the pre-exponential factor has been found to be $K = 1.68$.

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References

1. G. Camaggi and F. Gozzo, forthcoming paper.

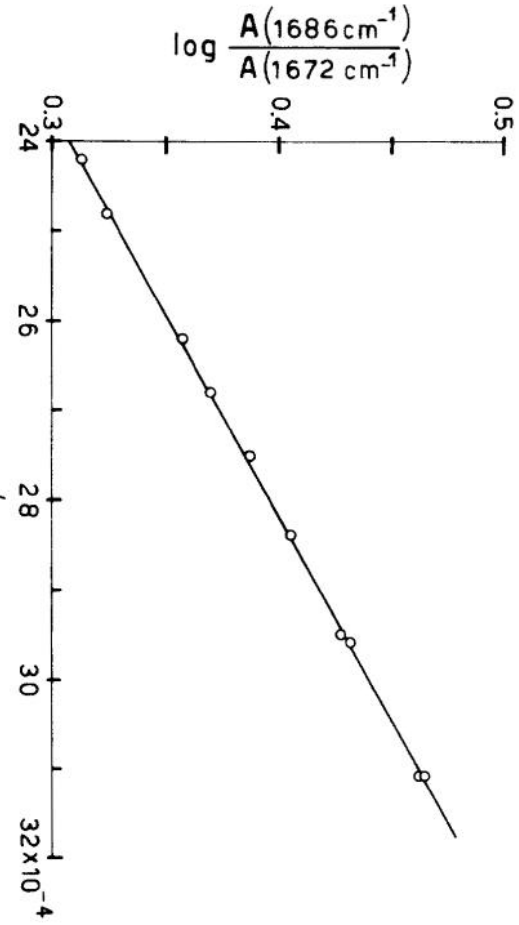

Fig. 1. Plot of $\log(A_{1686\ cm^{-1}}/A_{1672\ cm^{-1}})$ vs. 1/T for perfluoro(1-cyclohexylcyclohexene)