

Temperature Dependence of the Low-frequency Vibrational Optical Activity of α -Phellandrene

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Summary Dramatic changes with temperature in the Raman optical activity of two low-frequency vibrational bands of (–)- α -phellandrene, which could be associated with the interconversion of the pseudoaxial and pseudo-equatorial conformers, are reported.

It is well known that α -phellandrene shows an 'anomalous' optical activity that has been rationalized in terms of conformational mobility.¹⁻⁴ It is thought that the room temperature circular dichroism spectrum is dominated by a less stable pseudoaxial conformer, in which the diene unit of the (–)-enantiomer has a left-handed twist, which has a much larger long-wavelength rotational strength than the more stable pseudo-equatorial conformer where the diene unit has a right-handed twist. Here we report temperature-dependent Raman optical activity studies consistent with this interpretation. We refer to ref. 5 for a recent review of Raman optical activity.

We have constructed a cell which enables Raman optical activity spectra of liquids to be measured at temperatures in the range +150 to –160 °C. Here we present spectra from *ca.* 170 to 410 cm^{-1} at room temperature and at –60 °C. Even with this modest temperature difference large changes are seen in the Raman optical activity.

Figures 1(a) and (b) show the depolarized circular intensity sum and difference spectra of a 50% v/v solution of (–)- α -phellandrene in acetone at the two temperatures. There are two important features. First, a Raman band at 200 cm^{-1} with a significantly larger intensity at the higher temperature and a large negative optical activity at the higher temperature which disappears at the lower. Secondly, a Raman band at 276 cm^{-1} with a significantly larger intensity at the lower temperature and a large positive optical activity at the lower temperature which all but disappears at the higher.

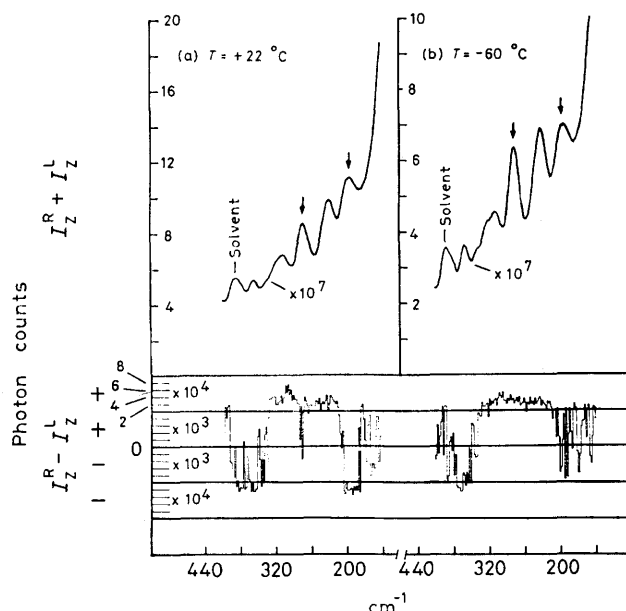


FIGURE 1. The depolarized Raman circular intensity sum and difference spectra of a 50% v/v solution of (–)- α -phellandrene in acetone at (a) 22 °C and (b) –60 °C. Experimental conditions: laser power 4.2 W, laser wavelength 488 nm, slitwidth 13 cm^{-1} , scan speed 1.0 $\text{cm}^{-1} \text{min}^{-1}$. The room temperature spectra were recorded in a standard fluorescence cell, path length = 10 mm. The low temperature spectra were recorded in a variable temperature cell, path length = *ca.* 5 mm.

The assignment of low-frequency skeletal vibrations in large molecules is usually difficult; the normal modes contain many internal co-ordinates, and the spectrum is complicated by hot bands. But in this instance the additional

Raman optical activity data suggests an interesting possibility for the 200 and 276 cm^{-1} bands. From the temperature dependence of the intensities, there is little doubt that the 200 and 276 cm^{-1} bands are associated with the less stable and more stable conformers, respectively. The fact that the intensity loss of one is approximately

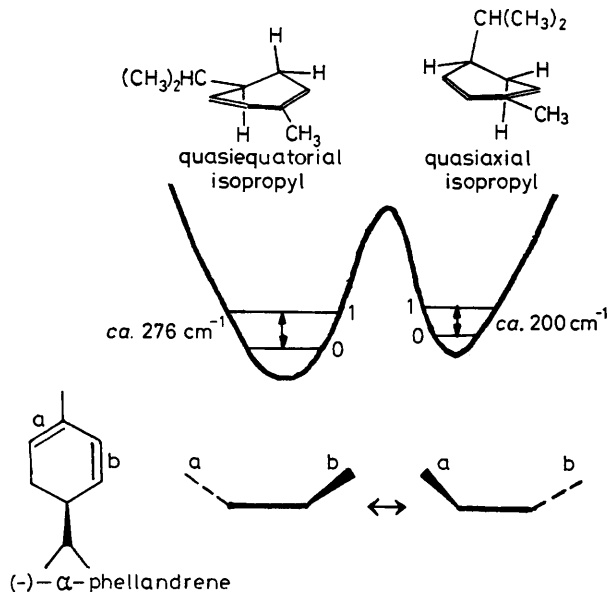


FIGURE 2. The double-well potential representing the interconversion pathway between the pseudoaxial and pseudoequatorial conformers of α -phellandrene.

balanced by the intensity gain of the other, and that they are associated with *opposite* optical activities, leads to the appealing interpretation that the two bands originate in 'enantiomeric' skeletal modes of the two conformers that are dominated by the diene torsion co-ordinate. These particular skeletal modes would correlate with each other *via* the co-ordinate describing the interconversion pathway between the two conformers, as illustrated in Figure 2. Since this vibration in the less stable conformer is associated with the shallower potential energy well, the corresponding fundamental vibrational transition would occur at the lower frequency, as observed.

Just as the less stable quasiaxial conformer dominates the room temperature circular dichroism, so for the proposed enantiomeric skeletal vibrational modes of the two conformers the associated Raman optical activity in the less stable conformer is larger than that in the more stable conformer. This probably follows from the allylic axial chirality effect⁶ where, for homoannular cisoid dienes, the chirality of the chromophore is the same as that imposed by the C-5 and C-6 pseudoaxial bonds on their respective adjacent double bonds (see Figure 2). The larger polarizability of C-CH(CH₃)₂ compared with C-H could account for the larger Raman optical activity associated with the pseudoaxial conformer.

It is emphasised that, although our suggested model fits the observations, it is speculative and there could be many complicating features.

We thank the S.R.C. for financial support.

(Received, 6th May 1981; Com. 534.)

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