Vibrational and rotational spectra and \textit{ab initio} calculations of thiocyanatoethene

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Raman spectra of thiocyanatoethene (TCE) as a liquid at various temperatures and of the amorphous and crystalline solids at liquid nitrogen temperature were recorded. IR spectra in the 4000-400 cm\(^{-1}\) region of the vapour, liquid, amorphous and crystalline solids at low temperature, and of the compound isolated in argon and nitrogen matrices at 5 K with the hot nozzle technique were obtained. Microwave spectra of TCE were recorded in the 10-39 GHz region employing Stark modulation. Areas of special interest were also investigated by use of the RFMWDR double resonance technique. \textit{Ab initio} calculations with different basis sets were carried out. The compound exists as a mixture of \textit{syn} and \textit{gauche} conformers in the vapour and liquid states, while the more stable \textit{syn} was present in the crystal. An enthalpy difference of 5.7(10) kJ mol\(^{-1}\) and a barrier of 8.4(3) kJ mol\(^{-1}\) was found.

1. INTRODUCTION

Only a few organic thiocyanates (R-SC=N) have been studied by vib-

rational spectroscopy and some conformational equilibria were reported in recent papers [1-4]. Very little work has

been done to characterise the physical properties of thiocyanates where the SCN-group is bonded to sp\(^2\) hybridised
carbon. Thiocyanatoethene is the simplest molecule in this group and it was expected that different conformers
exist due to rotation around the C(sp\(^2\)) - S bond. Preliminary Hartree-Fock \textit{ab initio} calculations (Figure 1) indicated
that two conformers exist: \textit{syn} (0\(^{\circ}\)) and \textit{gauche} (130/230\(^{\circ}\)).

![Torsional Potential of TCE](image_url)

Fig. 1. The \textit{ab initio} calculated torsional potential of TCE.
2. EXPERIMENTAL

The sample was synthesised by a slightly modified procedure to that previously described [5]. The IR, Raman and microwave spectrometers, the cryostats and the methods employed have been described in earlier papers [4,6,7].

3. RESULTS AND DISCUSSION

Both conformers have 18 vibrational modes and most of these were observed in the vapour and liquid phases. All the fundamentals of the syn conformer were found in the crystal, while the vapour phase wavenumbers for the two lowest fundamentals were estimated from intensity measurements of the first excited states in the microwave spectra (see later). The lowest out-of-plane fundamental vibration is found at slightly lower wavenumbers in the liquid and solid phases than estimated from the MW-spectra.

3.1. Vapour phase IR-spectra

The syn conformer is planar and belongs to the point group $C_\infty$. The vibrations of species $A'$ have contours which are hybrids of $A$- and $B$-type. The vibrations belonging to the species $A''$ give rise to pure $C$-type contours with very prominent $Q$-branches as are apparent from the IR vapour spectrum (Fig. 2). The gauche conformer has no elements of symmetry and belongs to the point group $C_1$. Therefore, hybrid type band shapes are observed in the vibrational spectra, as shown in Fig. 2. Theoretical vapour phase band contours of TCE are in good agreement with the experimental shapes.

3.2. Microwave spectrum and assignments

The microwave spectrum of the syn conformer in its ground vibrational state was easily assigned using the ab initio structural data. This conformer displays a semirigid-rotor spectrum with rotational constants: $A = 6689.312(14)$, $B = 3627.923(11)$ and $C = 2349.767(11)$ MHz. Spectral lines from three excited states were also assigned. The negative sign of the inertial defect of one of the states shows that it belongs to an out-of-plane motion, $v_{18}$. The other state has a positive inertial defect and is associated with an in-plane vibration, $v_{13}$.

Broad-band spectra taken in the 22 - 39 GHz region revealed a piled-up series of lines typical for a prolate asymmetric top. This series was assumed to belong to the gauche conformer. High resolution spectra of the pile-ups displayed an unusually dense and complex collection of transitions which demonstrates that several vibrationally excited states are present. Numerous unsuccessful attempts were made to fit these lines to a rigid-rotor model to within the expected experimental uncertainties. The best fits had r.m.s. deviations of several MHz. The reason for this is assumed to
be extensive vibration-rotation coupling, probably a consequence of a low double-
minimum barrier separating the two equivalent gauche forms. The best values of the
ground state rotational constants were: $A = 11496(74)$, $B = 2352.71(28)$ and $C =
2056.39(29)$ MHz.

3.3. Liquid and solid phase Raman spectra
Raman spectra of TCE in the liquid obtained at different temperatures are shown
in Fig. 3. The observed intensity changes of the liquid spectra with temperature and
a comparison with spectra of the crystal, show quite clearly that at least two con-
formers exist in the liquid. The enthalpy difference ($\Delta H^\circ$) between the conformers
was derived as 5.7(10) kJ mol$^{-1}$ with the syn conformer being the more stable.

The spectra of both an amorphous and a crystalline solid had bands which are
assigned solely to the syn conformer. The barrier between the two conformers is low
enough to allow interconversion in the amorphous solid at liquid nitrogen tempera-
ture, and only the low enthalpy syn conformer is accommodated in the crystal lattice.

3.4. IR matrix spectra
The population of the different conformers in the vapour phase was investigated
with the matrix isolation technique. TCE diluted in argon was heated to 300-900 K
using a hot nozzle, and the sample was shock frozen on a cold window (5-15 K). IR
matrix spectra in the C=N stretching re-
gion are shown in Fig. 4. Curves (a) give
the unannealed spectra at two nozzle
temperatures, curves (b) reveal the
effects of annealing. A band due to
matrix effects appears at 2175 cm$^{-1}$. The
enthalpy difference between the
conformers was estimated to be 3 - 6 kJ
mol$^{-1}$ from the relative intensities of the
bands at different nozzle temperatures,
with syn being the more stable
conformer. The matrix effects disappear
around 24 K and the gauche conformer
interconverts to syn above 27 K.

The barrier between the conformers
has been estimated by calculating the
rate constant of the interconversion and
employing the method of Barnes [8].
This gives a value of 8.4(3) kJ mol$^{-1}$
which compares well with the 6-31G* ab
initio result.
Fig. 4. IR spectra of TCE isolated in an argon matrix: a) at two different nozzle temperatures; b) after annealing to different temperatures.

4. CONCLUSIONS

The observed enthalpy difference between the conformers (syn being the more stable in all phases) differ from the values obtained from ab initio Hartree-Fock calculations. Calculations with the 6-31G* basis set even suggest that gauche is the more stable conformation. Apparently, the calculations should be carried out with larger basis sets and include electron correlation in order to give more reliable enthalpy differences for this class of compounds. However, the 6-31G* calculations give force constants which after appropriate scaling reproduce the experimental syn and gauche bands quite well.

The existence of the gauche conformer is rather unexpected judging from the literature. The X-ray studies of two other rather large aliphatic sp² hybridised organic thiocyanates [9] conclude that the anti conformation is present in the crystal.

REFERENCES