# Rotational isomerism and vibrational spectra of 3-chloro 1-butene

J. N. SOM AND G. S. KASTHA

*Department of Optics, Indian Association for the Cultivation of Science*

*Jadavpur, Calcutta-700032*

The Raman spectra of 3-chloro 1-butene in the liquid phase at different temperatures, its infrared absorption spectrum at room temperature and intensity variation of some Raman lines within a limited temperature range have been studied. The results indicate that the molecules of this compound in the liquid phase exist in three rotationally isomeric forms which are identified as the $cis_1$, $cis_2$ and $trans_1$ conformer. It is also observed that the forms $cis_1$ and $cis_2$ are of almost equal energy content in the liquid phase A probable assignment of all the observed vibrational frequencies of the molecule has been proposed.

## 1. INTRODUCTION

Molecules of alkenes and haloalkenes, because of internal hindered rotation, can exist in different rotationally isomeric configurations similar to those occuring in the corresponding alkanes and haloalkanes. In the case of the former molecules whose rotamers are, generally, described with respect to the $=CH_2$ group, the cis form is one of the stable conformations unlike in the latter cases. For example, in 1-butene (3-methyl propene) the more stable form has been found to be the cis-configuration (Kondo et. al. 1968) while of the three possible conformers cis, trans and gauche for the molecule of allyl chloride (3-chloropropene) the cis-form has been identified as one of the conformers in the liquid state (Pentin & Sharipov 1963, Mclachlan & Nyquist 1968). In methallyl chloride spectroscopic results (Pentin & Morozov, 1966) indicate the presence of the cis, the trans and an approximate gauche conformer in the liquid phase.

In the molecule of 3-chloro 1-butene obtained by the replacement of one hydrogen atom of the third carbon of 1-butene by a chlorine atom, internal rotation about the 2, 3 carbon-carbon bond is expected to give rise to several possible conformations. The present investigation on the Raman and Infrared spectra of the compound was undertaken in order to identify these rotamers in the liquid phase. The results and their discussions are presented in this communication.

J. N. Som and G. S. Kastha

## 2. EXPERIMENTAL AND RESULTS

Raman spectra of the compound in the liquid state at different temperatures were photographed with the Fuess glass spectrograph as usual. Laser Raman spectra in the liquid state in the temperature range 30°C–60°C were also obtained using the Argon Ion 4880 Å as the exciting radiation. The solid state Raman spectrum at 93°K was also investigated. Infrared absorption spectrum of the pure liquid in the region 600–1800cm$^{-1}$ was recorded on a Perkin-Elmer Model 21 Spectrophotometer with rocksalt optics.

The wave number of the Raman shifts and the infrared absorption bands are given in table 1. Assignments proposed for the vibrational frequencies are included in the last column of the table.

Table 1. Infrared and Raman spectra of 3-chloro 1-butene

| IR bands(cm$^{-1}$) Liquid | Raman Shifts(cm$^{-1}$) | | Assignments |
| --- | --- | --- | --- |
| | Liquid | Solid | |
| | 108 (4) | | Torsion |
| | 176 (½) | | |
| | 289 (1) | | $\delta$(C—C—Cl) |
| | 315 (½) | | $\delta$(C·C—C) |
| | 357 (10) | 357 (1) | $\delta$(C—C—Cl) / $\delta$(C—C—C) |
| | 461 (4) | 454 (½) | $\delta$(C=C—C) / $\delta$(C—C—C) |
| | 495 (2) | | $\delta$(C=C—C) |
| | 598 (1) | | (C=C) twist |
| | 631 (2) | | |
| 676 (m) | 673 (10b) | 670 (2) | $\nu$(C—Cl) cis$_1$ |
| 707 (s) | 707 (6) | | $\nu$(C—Cl) cis$_2$ |
| 752 (w) | | | $\nu$(C—Cl) trans$_2$ / gauche |
| 783 (m) | 783 (6) | 779 (½) | $\nu$(C—Cl) trans$_1$ |
| 863 (m) | 862 (2) | | CH$_3$ rock |
| 933 (vs) | 937 (½) | | $\nu$(C—C) / C=CH$_2$) Wag (out of plane) |
| 969 (vs) | | | $\nu$(C—C) |
| 992 (s) | 980 (½) | | (—CH=CH—) Wagging, out of plane |

Table 1 (*Contd.*)

| IR bands(cm⁻¹) Liquid | Raman Shifts(cm⁻¹) | | Assignments |
|---|---|---|---|
| | Liquid | Solid | |
| 1027 (s) | 1031 (1) | | $\nu$(C—C) |
| 1076 (m) | 1083 (3) | | (—CH$_2$) rock in plane |
| 1156 (w) | | | CH$_3$ rock |
| 1178 (m) | 1180 (5) | 1180 (½) | (—CH$_2$) rock in plane |
| | 1219 (1) | | (CH) deformation |
| 1241 (s) | | | (CH) deformation |
| 1260 (vs) | 1259 (5) | 1245 (0) | (CH-CH—) bending in plane |
| 1282 (w) | | | (—CH=CH—) bending in plane |
| 1315 (w) | 1313 (6b) | 1308 (½) | CH Wag |
| 1384 (s) | 1383 (1) | | CH$_3$ berding symm |
| 1424 (sh) | 1418 (½) | | (—CH$_2$) bending in plane |
| 1454 (vs) | 1460 (5b) | | CH$_3$ bending assym |
| | 1639 (6) | 1639 (0) | $\nu$(C=C) cis$_2$ |
| 1653 (m) | | | $\nu$(C=C) trans$_1$ |
| 1673 (m) | 1669 (8) | 1664 (1½) | $\nu$(C C) cis$_1$ |
| | 2863 (3) | | $\nu$(C—H) symm in (CH$_3$) |
| | 2920 (6) | | $\nu$(C—H) in (—CH) |
| | | | $\nu$(C—H) in (CH$_3$) assym. |
| | 2960 (4) | | $\nu$(C—H) in (CH$_3$) assym. |
| | 2992 (3) | | $\nu$(C—H) sym in (=CH$_2$) |
| | 3031 (4) | | $\nu$(C—H) in (=CH) |
| | 3095 (2) | | $\nu$(C—H) assym in (=CH$_2$) |

## 3. DISCUSSIONS

**Existence of rotational isomerism.**

The probable five configurations of the molecule of 3-chloro 1-butene are illustrated in figure 1. From comparisons with the possible conformations reported for the molecules of 3-halopropene, 2-methyl 1-butene (Shimanouchi et. al. 1968) and 1-butene the first three forms designated cis$_1$, cis$_2$ and trans$_1$

(figure 1) are expected to be the more probable conformers present in the liquid state.
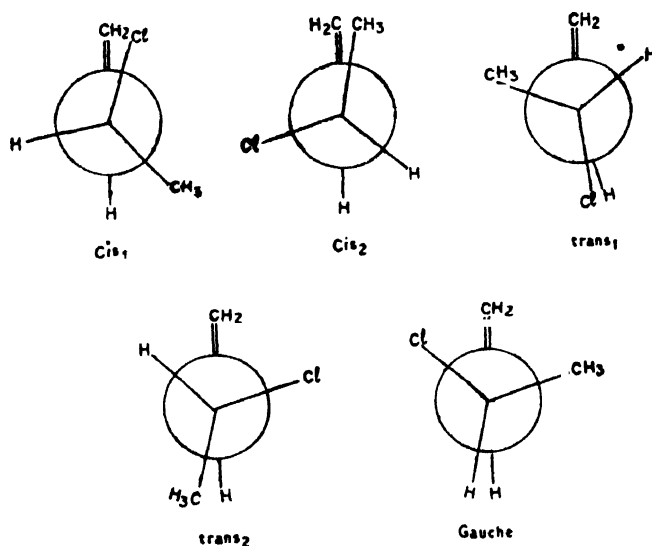


Fig. 1. Conformers of 3-chloro 1-butene.

It is seen from table-1 that the total number of distinct Raman and infrared frequencies observed with the compound in the liquid state, specially those appearing in the frequency regions representing (C = C) stretching, (C — Cl) stretching and the skeletal deformation vibrations, is larger than the total number of fundamental vibrational frequencies possible for a single conformer of the molecule. The (C = C) stretching frequencies for olefins lie between 1640-1680cm⁻¹ and in the liquid phase spectra of the present compound, there are two strong Raman lines at 1669 and 1639 cm⁻¹ and two infrared bands at 1673 and 1653cm ¹. The three bands 1669, 1653 and 1639 cm⁻¹ in all probably represents the ν (C=C) vibrations in the different conformers of the molecule. Similarly in the C-Cl stretching vibration region, which in halogenated olefins lies in the region 650–800 cm⁻¹, three strong Raman lines at 673, 707 and 783cm⁻¹ and corresponding infrared bands at 676, 707 and 783cm⁻¹ have been observed. Besides, there is a weak band at 753cm⁻¹ in the ir spectrum of the liquid. All these frequencies most probably represent the (C-Cl) strething vibrations in the different conformers of the molecules. Since for a single conformer the vibrational spectrum should exhibit only one characteristic frequency due to each mode of vibration, the presence of several (C = C) and (C-Cl) stretching frequencies in the liquid phase spectra suggests the existence of at least three conformers of the molecule of the compound.

### Identification of the rotamers.

*(C=C) stretching vibrations.* Only one frequency due to $C=C$ stretching vibration for each of the molecules of propylene, 1-butene and 3-methyl 1-butene (Sheppard & Simpson, 1952) have been observed at 1648, 1639 and 1642cm$^{-1}$ respectively while in the case of 3-chloro propene (Mclachlan & Nyquist 1968) there are two frequencies at 1649 and 1642cm$^{-1}$ which have been assigned respectively to the cis- and gauche-forms of the molecule. It has been pointed out by these authors that the presence of the heavy chlorine atom in the position cis to the $=CH_2$ group in the latter molecule is responsible for the occurrence of two $\nu$ (C=C) frequencies in contrast to the only one such frequency observed in the case of the former molecules, where the $CH_3$ group is cis to the $=CH_2$ group. From these considerations the frequency 1639cm$^{-1}$ is attributed to the cis$_2$ form where the $CH_3$ is cis to $=CH_2$ group and the highest frequency 1669cm$^{-1}$ is assigned to the cis$_1$ form. The remaining frequency 1653cm$^{-1}$ is most probably due to the trans$_1$ form.

### (C—Cl) stretching vibration

Mclachlan and Nyquist (1968) observed only one frequency at about 736cm$^{-1}$ for the molecule of allyl chloride and assigned it to the gauche conformer. But two C-F stretching frequencies were observed in the case of allyl flouride and the $\nu$(C–F) frequency for the cis rotamer was found to be less than that for the gauche. Pentin & Morozov (1966) showed that the $\nu$(C-Cl) for the cis-conformer will be lower than that for the trans form. Thus it is seen that in each of these cases the C-Hal stretching frequency for the cis-rotamer has a value lower than that in any other conformer. Hence of the frequencies 783, 707 and 673cm$^{-1}$ representing the $\nu$(C-Cl) vibrations in different conformers of 3-chloro 1-butene the lowest frequency 673cm$^{-1}$ in definitely attributable to the cis$_1$ form, while the frequencies 707 and 783cm$^{-1}$ will most probably represent such vibration in the cis$_2$ and trans$_1$ form respectively. The weak infrared band at 753cm$^{-1}$ may represent the (C-Cl) stretching vibration in one of the other two remaining conformers (trans$_2$ and gauche). But this assignment is not very certain.

### (C = C) twist vibrations.

Harrah & Mayo (1960) observed two frequencies at 634 and 552cm$^{-1}$ due to ethylinic twisting vibrations in the two rotamers of a number of 1-alkene compounds. Also in the molecule of 3-chloropropene the bands 590 and 550cm$^{-1}$ have been assigned to C = C twisting mode in the gauche and cis forms. In the present case two Raman lines at 631 and 598cm$^{-1}$ have been observed in the spectrum of the compound in the liquid state and they are

attributed, by comparison, to the C = C twisting modes. Thus, by the way, indicates the existence of more than one conformer in the liquid state of the compound.

### Stability of the rotamers.

The Raman specra in the liquid phase at 10°C, 30°C and 60°C have been photographically obtained. Visual comparison of the spectra indicates that of the pair of Raman lines 1639 and 1669cm⁻¹ the relative intensity of the latter decreases with increase of temperature. This points to the fact that the cis₁ conformer is the more stable configuration in the liquid state.

Inspite of repeated attempts it has not been possible to obtain a perfectly crystalline form of the compound. Cooling and annealing of the sample always yield an amorphous solid whose spectrum at −180°C contained a very few Raman lines greatly reduced in intensity The presence of the Raman lines 1669cm⁻¹ and 673cm⁻¹ could, however, be detected thereby indicating that the cis₁ form is also a stable form in this case.

### Energy difference.

Attempts were made to determine the energy difference between the two conformers from measurements of the temperatuie dependence of the ratio of relative intensities of the lines 1669cm⁻¹ and 1639cm⁻¹ in the limited temperature range (30-60°C), because of low boiling point of the compound. The results which qualitatively support the conclusions of the visual observation indicate that the two forms cis₁ and cis₂ are of nearly energy content.

### Assignment of other vibrational frequencies.

The assignments of vibrational frequencies of =CH₂, =CH, CH₃ and CH groups and the skeletal (C–C) stretchings have been made from straight forward comparisons with the molecules of propylene, 1-butene and allyl chloride. Majority of these frequencies are due to coinciding vibrational modes of the different conformers of the compound. These assignments are shown in table 1 without indicating the particular conformers to which such modes may belong. However, the assignments of the v(C-Cl) and v(C=C) frequencies have been made in represent of the modes of the probable conformers and are indicated in the table.

In the liquid phase Raman spectrum there are eight Raman lines in the region 100–500cm⁻¹. These frequencies are due to skeletal deformation modes in different conformers. The assignments which are tentative refer only to the general modes of vibration.

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# BOOK REVIEW

X-ray Diffraction Topography, by B. K. Tanner, Vol. 10 of the International
Series in the Science of the Solid State, Pergamon Press, flexicover edn.
(£ 6.25), 1976.

As far as the present reviewer's knowledge goes, probably this is the
first well-written and comprehensive book on the celebrated field of X-ray
diffraction topography, which took a new dimension with the well-known work
performed by A. R. Lang in the year 1958 although the pioneering work on
topography was done by the noted Indian scientist G. N. Ramachandran in
the year 1944. In the past years, the works on X-ray topography were mainly
described in pages of several journals, in technical reports, in a few review
articles (by Lang and others), in conference volumes and in small chapters
of text books on solid state physics and materials science. As such, this
book is certainly 'assured of a ready welcome' to large number of workers
devoted to fundamental and applied work on solid state physics and solid
state devices. X-ray diffraction topography, a relatively new and powerful
tool to study crystal imperfections in a non-destructive manner, is comple-
mentary to the widely used method of transmission electron microscopy (TEM),
and is receiving attention in recent years not only from the X-ray diffrac-
tionists to unravel many new fundamental X-ray optical phenomena and the
various implications of dynamical diffraction theory for perfect crystals but
also from crystal growers and device manufacturers in the electronic industry
who are trying for the quality control of the monolithic crystal devices.

The book contains seven chapters and is primarily divided into three
sections. The first section concerns the basic dynamical X-ray diffraction
theory (chapt. 1), the principal experimental techniques (chapt. 2) namely,