

CONFORMATIONAL STRUCTURE  
AND VIBRATIONAL SPECTRA  
OF 2,4-DICHLORO-2,4-DIMETHYLPENTANE  
AND 4-CHLORO-2,2,4-TRIMETHYLPENTANE

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Infrared and Raman spectra of 2,4-dichloro-2,4-dimethylpentane and 4-chloro-2,2,4-trimethylpentane were measured in the temperature range  $-130$  to  $+60^{\circ}\text{C}$  and the stable conformers were determined.

Ranges where absorption bands of C—Cl stretching vibrations appear in different conformers of linear hydrocarbons containing a tertiary chlorine atom have been determined by Mizushima<sup>1</sup> and by Shipman and coworkers<sup>2</sup> who studied the infrared spectra of liquid samples of these compounds. Energy differences between various conformers of 3-chloro-3-ethylpentane<sup>3</sup> have been determined from the temperature dependence of infrared and Raman spectra. A very detailed analysis of this region in vibrational spectra of cyclic compounds has been presented by Altona and coworkers<sup>4</sup>.

In all the previous studies, compounds containing only one tertiary carbon atom have been investigated. For the elucidation of conformational preferences in some polymers, the conformational structure of molecules with two tertiary chlorine atoms in 1,3-position is of importance. We have studied the conformational structure of the simplest compound of this type, 2,4-dichloro-2,4-dimethylpentane, in solid and liquid state by infrared and Raman spectra. Besides this, 4-chloro-2,2,4-trimethylpentane was also studied as a conformationally simpler model.

#### EXPERIMENTAL

*4-Chloro-2,2,4-trimethylpentane* (compound A). Compound A was prepared by reaction of dry gaseous HCl with diisobutylene and precipitated by cooling according to Whitmore<sup>5</sup>. The product was washed with water to neutral reaction and dried over  $\text{K}_2\text{CO}_3$ . The fraction boiling at  $44^{\circ}\text{C}/16$  Torr was isolated by vacuum distillation. Product:  $n_D^{20}$  1.4314 (ref.<sup>5</sup>  $n_D^{20}$

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1.4307), found: 64.77% C, 11.60% H, 24.14% Cl; calculated: 64.63% C, 11.52% H, 23.85% Cl, m.p.  $-32^{\circ}\text{C}$ .

2,4-Dichloro-2,4-dimethylpentane (compound B). Compound B was prepared by reaction of concentrated HCl with 2,4-dimethylpentane-2,4-diol under vigorous stirring and cooling by ice with salt<sup>6</sup>. After 2½ h the product was isolated and washed by a 2% solution of NaHCO<sub>3</sub> and several times with ice water to neutral reaction. The product was dried over CaCl<sub>2</sub>. The fraction boiling at 60–62°C/10 Torr was isolated by vacuum distillation. 2,4-Dimethylpentane-2,4-diol was prepared by Grignard synthesis with CH<sub>3</sub>MgI from diacetone alcohol according to Frank-Kohn<sup>7</sup>. The unreacted diacetone alcohol was removed by the action of NaHSO<sub>3</sub> for 50 h. Diacetone alcohol was obtained by condensation of acetone in the presence of BaOH<sub>2</sub> (ref.<sup>8</sup>): Compound B was purified by double crystallization from CS<sub>2</sub> 10% solution at  $-78^{\circ}\text{C}$ . Product:  $n_{\text{D}}^{20}$  1.4532 (ref.<sup>9</sup>  $n_{\text{D}}^{20}$  1.4537), m.p. 26–27°C.

The reaction of both compounds was neutral. The purity of both samples was controlled by infrared and NMR spectra, proving the absence of double bonds. During prolonged measurement at room temperature, sample A decomposed very slowly, as demonstrated by the appearance of a weak band of a double bond in the infrared spectrum.

Infrared spectra were measured in the range 400–3500 cm<sup>-1</sup> on the Zeiss UR-10 spectrometer, in the range 250–400 cm<sup>-1</sup> on the Perkin-Elmer Infracord Type 457. The temperature dependence of the spectra in the range  $-130$  to  $40^{\circ}\text{C}$  was recorded in a special variable temperature cell without entrance and exit windows<sup>10</sup>. Dichroism of the lines in samples crystallizing with a certain degree of orientation was measured in the same cell by means of an AgCl polarizer.

Raman spectra were measured on the DFS-12 spectrometer, with a He–Ne laser (30 mW) as excitation source. The temperature dependence of Raman spectra in the range  $-130$  to  $60^{\circ}\text{C}$  was measured in a variable temperature cell of our own construction<sup>11</sup>.

## RESULTS

If only staggered conformers are considered, then compound A can form two (Fig. 1) and compound B four different rotational isomers (Fig. 2). These conformers differ by symmetry and type of chlorine atoms. The types of chlorine atoms in various conformers are indicated in Figs 1 and 2, using the conventional nomenclature.\*

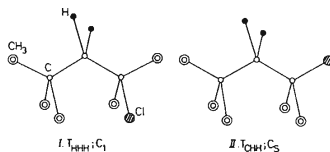


FIG. 1

Rotational Isomers of 4-Chloro-2,2,4-trimethylpentane

\* The letter T designates a tertiary chlorine atom and the indexes H and C designate the atoms which are in *trans* position with respect to chlorine.

Infrared and Raman spectra of compound A measured in liquid and solid state are shown in Figs 3–5, infrared and Raman spectra of compound B are shown in Figs 5–7. In both compounds, some lines are seen to “freeze out” upon transition into the solid state. In compound B we have succeeded in growing oriented crystals in the infrared cell, making thus possible a determination of the dichroism of the lines (Fig. 8). In both compounds, the temperature dependence of infrared and Raman spectra has been followed from +60 to  $-130^{\circ}\text{C}$ ; from these measurements, the energy differences between some conformers could be determined.

In the range of C—Cl stretching vibrations, infrared and Raman spectra of compound A in the liquid state exhibit three bands at 540, 587 and  $633\text{ cm}^{-1}$ . In the solid state, the band at  $633\text{ cm}^{-1}$  disappears. Liquid compound B exhibits in this region 5 bands at 532, 574, 596, 647 and  $677\text{ cm}^{-1}$ . In the solid state, two lines disappear and only the bands at 532, 568 and  $588\text{ cm}^{-1}$  remain.

Infrared spectra of compound B crystallized between cell windows exhibit different band intensities according to the conditions of cooling. Two extreme cases are shown in Fig. 9. Crystallization of the sample in a KBr pellet yields always the same kind of spectrum (Fig. 6). From this it is evident that band intensity differences are determined by a different degree of crystal orientation.

## DISCUSSION

*Compound A.* As seen from Fig. 1, compound A can exist in two conformational forms. Conformer I has a  $T_{\text{HHH}}$  type chlorine atom, with an expected band below

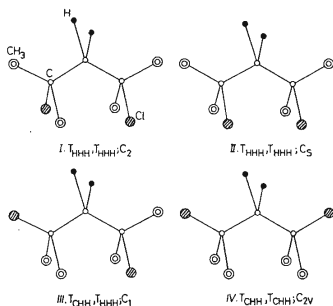


FIG. 2  
Rotational Isomers of 2,4-Dichloro-2,4-dimethylpentane

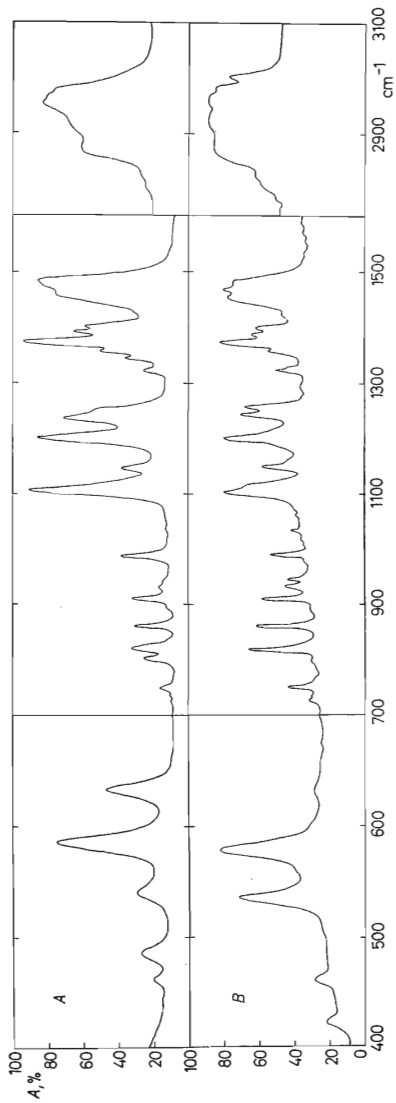


FIG. 3  
Infrared Spectra of 4-Chloro-2,2,4-trimethylpentane  
A Liquid, B solid state.

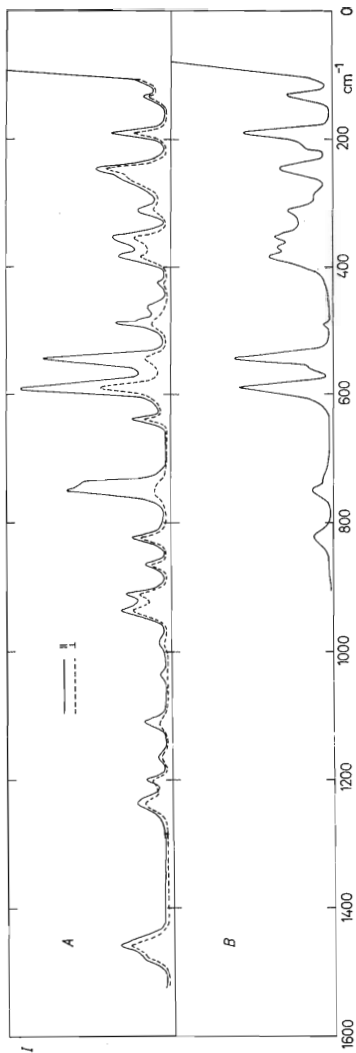


FIG. 4  
Raman Spectra of 4-Chloro-2,2,4-trimethylpentane  
A Liquid, B solid state.

600  $\text{cm}^{-1}$ , and conformer *II* has a  $T_{\text{CHH}}$  type chlorine, with an expected band above 600  $\text{cm}^{-1}$ . The band at 633  $\text{cm}^{-1}$ , disappearing upon crystallization of compound *A*, evidently belongs to conformer *II*. In the range of C—Cl stretching vibrations, two bands remain unchanged in the solid state. Of these, the band at 587  $\text{cm}^{-1}$  corresponds to conformer *I*. The band at 540  $\text{cm}^{-1}$  could be assigned to a  $T'_{\text{HHH}}$  type C—Cl stretching vibration, or to a skeletal C—C—C bending vibration with intensity enhanced by interaction with the C—C—Cl angle. In compound *A* the structure  $T'_{\text{HHH}}$  cannot exist. A band at this frequency appears also in other compounds with a tertiary chlorine atom which likewise cannot appear in the form of a conformer with a  $T'_{\text{HHH}}$  chlorine atom. In variable temperature measurements of compound *A* the band at 540  $\text{cm}^{-1}$  exhibits the same behaviour as other bands typical of conformer *I*; we therefore assume compound *A* in the solid state to contain only one conformer with a single C—Cl stretching vibration at 587  $\text{cm}^{-1}$ .

The band at 540  $\text{cm}^{-1}$  has also been observed by Altona and coworkers<sup>12</sup> who explain its origin by Fermi resonance between the C—Cl stretching vibration and a harmonic of a bending vibration lying around 280  $\text{cm}^{-1}$ . In our compound this explanation seems improbable because no band appears around 280  $\text{cm}^{-1}$  in the solid state, neither in the infrared, nor in the Raman spectrum.

From the temperature dependence of the intensities of the bands at 587 and 633  $\text{cm}^{-1}$ , the energy difference  $\Delta E = 0.3$  kcal/mol has been calculated under the assumption that the absorbances are independent of temperature.  $\Delta E$  has also been calculated from the pairs of lines 462, 487 and 804, 820  $\text{cm}^{-1}$ . The same value was obtained in all cases. In the infrared and Raman spectra of compound *A* measu-

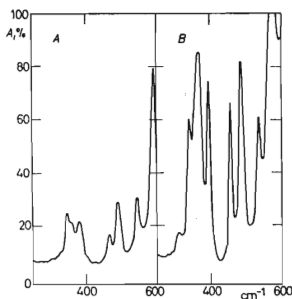


FIG. 5

Infrared Spectra in the Region 250—600  $\text{cm}^{-1}$

A 4-Chloro-2,2,4-trimethylpentane, B 2,4-dichloro-2,4-dimethylpentane.

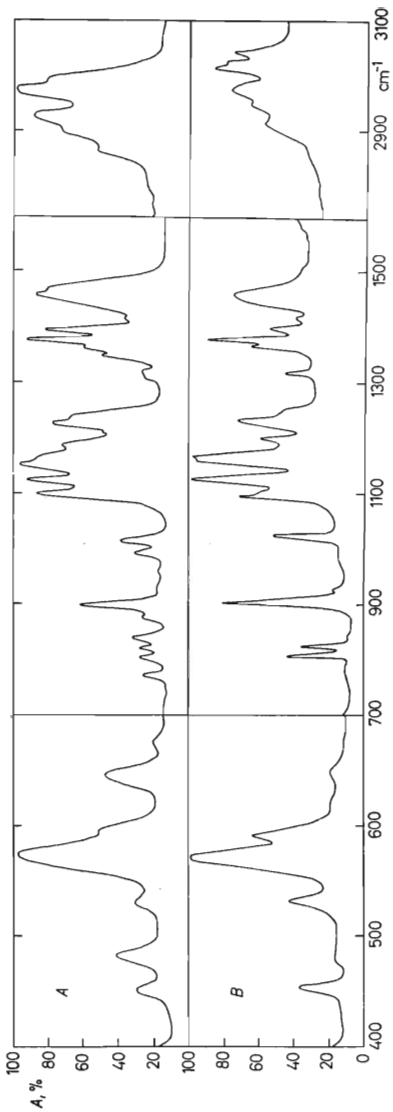


FIG. 6

Infrared Spectra of 2,4-Dichloro-2,4-dimethylpentane  
A Liquid, B solid state.

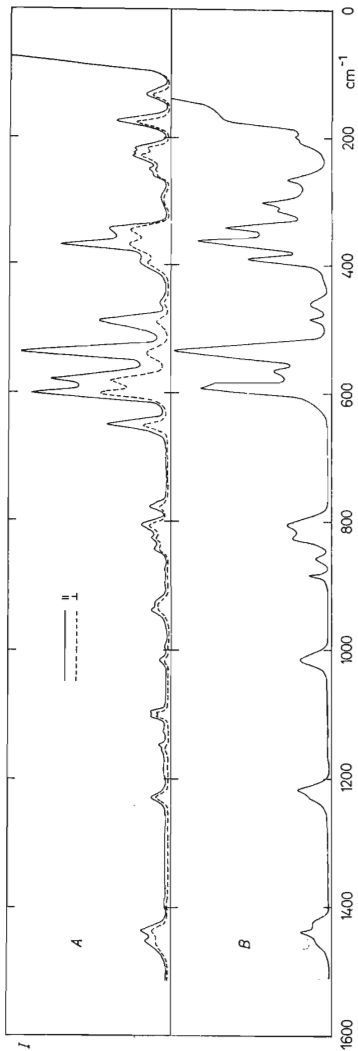


FIG. 7 Raman Spectra of 2,4-Dichloro-2,4-dimethylpentane A Liquid, B solid state.

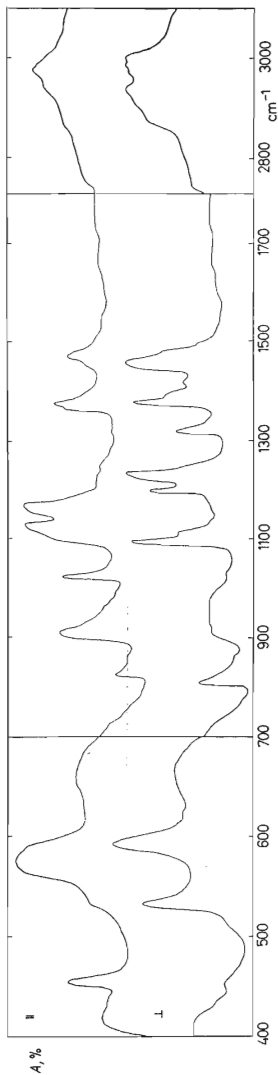


FIG. 8 Infrared Spectra of Oriented Crystals of 2,4-Dichloro-2,4-dimethylpentane



red in the liquid state, no other bands indicating the presence of further conformers have been found.

**Compound B.** Of the possible conformers of this compound shown in Fig. 2, forms *I* and *II* contain only  $T_{HHH}$  type chlorine atoms, so that C—Cl stretching bands can be expected to appear between 550 and 600  $\text{cm}^{-1}$ . Conformers *III* and *IV* with  $T_{CHH}$  type chlorine atoms should exhibit bands above 600  $\text{cm}^{-1}$ . Because during crystallization the bands above 600  $\text{cm}^{-1}$  “freeze out” and of the C—Cl stretching vibrations only the bands at 532, 568 and 588  $\text{cm}^{-1}$  remain in solid state, it is evident that conformer *I* or *II*, or both are present in the solid. Similarly as in compound A, the band at 532  $\text{cm}^{-1}$  is assigned as a skeletal deformation vibration. The bands at 568 and 588  $\text{cm}^{-1}$  have a definitely opposite dichroism, which is expected for the antisymmetrical and symmetrical vibrations of conformers *I* or *II*. It is improbable that such a well defined dichroism would appear, if both conformers were present in the solid state. Dempster and Sheppard<sup>13</sup> have shown that conformers with parallel C—Cl bonds in 1,3 position are energetically strongly unfavoured. We therefore assume that compound B in the solid state contains only conformer *I*. The different intensity ratio of bands in Raman and infrared spectra indicates that the line at 588  $\text{cm}^{-1}$  is a symmetrical C—Cl stretching vibration, and the band at 568  $\text{cm}^{-1}$  is the corresponding antisymmetrical vibration. In the infrared spectrum, the band at 568  $\text{cm}^{-1}$  is split, probably due to oriented intermolecular forces of the crystal lattice.

In vibrational spectra of compound B measured in the liquid state, the band at 647  $\text{cm}^{-1}$  indicates the presence of a conformer with a  $T_{CHH}$  type chlorine atom. This type of chlorine atom appears in conformers *III* and *IV*. Similarly as in com-

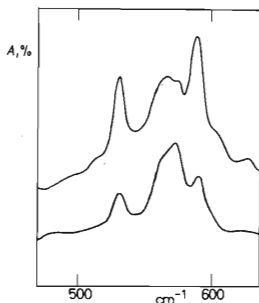


FIG. 9

Infrared Spectra of 2,4-Dichloro-2,4-dimethylpentane in Solid State

pound A, conformer *III* may be expected to be more favoured, and we therefore assign this band predominantly to the C—Cl stretching vibration of conformer *III*. In addition to the  $T_{\text{CHH}}$  type chlorine atom, this conformer also contains a  $T_{\text{HHH}}$  type chlorine, and it must therefore exhibit also a band below  $600\text{ cm}^{-1}$ . This band probably overlaps the band of the antisymmetric C—Cl stretching vibration of conformer *I* ( $574\text{ cm}^{-1}$ ). This follows partly from the relatively low value of the depolarization factor, which is equal to 0.6 (for an antisymmetric vibration expected around 0.85), partly from the striking increase of intensity upon melting.

The very weak line at  $677\text{ cm}^{-1}$ , polarized in the Raman spectrum, could be a symmetrical C—Cl stretching vibration of conformer *IV*. In secondary chlorides with an analogous arrangement of chlorine atoms<sup>14</sup>, the symmetrical stretching vibration interacts with skeletal vibrations and is thereby shifted to higher frequencies by about  $40\text{ cm}^{-1}$ . The position of the band at  $677\text{ cm}^{-1}$  shows that such an interaction may also occur in tertiary chlorides. The antisymmetrical C—Cl stretching vibration of conformer *IV* may be expected in the frequency range of  $T_{\text{CHH}}$  type chlorine atoms, i.e. around  $640\text{ cm}^{-1}$ .

Assuming that most of the intensity of the band at  $640\text{ cm}^{-1}$  is due to conformer *III* of compound B, the energy difference  $\Delta E$  between conformers *I* and *III* has been calculated from the temperature dependence of the Raman lines at  $647$  and  $596\text{ cm}^{-1}$ , and found equal to  $0.5\text{ kcal/mol}$ .

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