# Infrared and Raman Spectra and Rotational Isomerism of 1,4-Pentadiene

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Rotational isomerism of 1,4-pentadiene has been studied. Normal frequencies have been calculated for the low frequency vibrations of four possible rotational isomers. From the change in the spectra in the gaseous, liquid, glassy, and solid states, it has been concluded that the two skew-skew forms (SS and SS′) and the *cis*-skew form (CS) are stable in the liquid and gaseous states, the SS and SS′ forms coexist in the glassy state, and only the SS form remains in the solid state. It has also been found that the energy difference among the three isomers in liquid state is not appreciably large.

The rotational isomerism about the C–C bond adjacent to the C=C double bond has been studied by several authors. Harrah and Mayo suggested the existence of rotational isomers of 1-olefins from the infrared spectra.[1] Kondo, Hirota, and Morino analyzed the rotational spectra of 1-butene and determined the structures of the *cis* and skew isomers, the latter being obtained from the *cis* form by an internal rotation of about 120°.[2] Shimanouchi, Abe, and Alaki studied the skeletal deformation vibrations of 1-olefins in relation to the stable conformations of 1,4-polybutadiene chains. They concluded that the *cis* and skew conformations are stable for the C–C bond neighbouring the *trans* C=C bond, whereas only the skew conformation is stable for the C–C bond adjacent to the *cis* C=C bond.[3]

As an extension of such a work, we have studied the molecular conformations of 1,4-pentadiene in the gaseous, liquid, and solid states by analyzing the infrared and Raman spectra. After our work had been completed, we found a paper by Gallinella and Cadioli, which treated the same subject by means of Raman spectroscopy and *ab initio* MO calculations.[4] Although their conclusion about the conformations of the stable isomers in liquid is consistent with ours, there seems to be significant differences regarding the assignments of bands to each isomer. In this paper we will describe the band assignments based on our experimental results and normal vibration calculations.

## Experimental

1,4-Pentadiene(Tokyo Chemical Industry Co.) was used without further purification for the measurement of the infrared spectra. The sample was distilled *in vacuo* prior to measurement of the Raman spectra. The infrared spectra were recorded on a Hitachi EPI-L double beam grating spectrometer in the region 700—300 $cm^{-1}$, and on a Hitachi FIS-1 double beam vacuum grating spectrometer in the region 500—200 $cm^{-1}$. The spectra in the gaseous state were taken with a 10 cm cell in the region 700—200 $cm^{-1}$ and a 4.9 m multireflection cell with polyethylene windows in the region 400—200 $cm^{-1}$. We measured the spectrum in the liquid state for the thin film obtained by warming up the solid film deposited on a cooled KRS-5 plate just above the melting point. The glassy solid was obtained by the deposition of the sample on a cooled window of KRS-5 or silicon. For the spectrum in the crystalline state, the sample was repeatedly annealed until no further spectral change was observed. The Raman spectra were measured on a JRS-400D spectrophotometer with a Coherent Radiation CR-3 argon ion laser as the light source. A multireflection accessary was used for the measurement of the spectrum of gaseous state.

## Results and Discussion

*Infrared and Raman Spectra and Rotational Isomerism.* The infrared and Raman spectra of 1,4-pentadiene in the gaseous, liquid, and solid states are shown in Figs. 1 and 2. The Raman spectra in the liquid and solid states are just the same as those reported by Gallinella and Cadioli.[4] The results so far obtained for the rotational isomerism about the C–C axis adjacent to the C=C bond show that the stable conformations are always *cis* and skew.[2,3] Since 1,4-pentadiene has two C–C axes, four isomers, SS, SS′, CS, and CC (Fig. 3) are considered to exist. Because of the steric repulsion between the terminal $CH_2$ groups in the CC form, the existence of this isomer is unlikely. Thus, the SS, SS′, and CS forms are the possible stable isomers. For each isomer, two CH out-of-plane vibrations and three skeletal deformation vibrations are expected in the regions 700—500 $cm^{-1}$ and 500—200 $cm^{-1}$, respectively.[3] Thus the five Raman lines observed at 672, 618, 457, 376, and 318 $cm^{-1}$ in the crystalline state (Fig. 2d) are reasonably assigned to one isomer. In the infrared spectra, the bands at 444 and 306 $cm^{-1}$

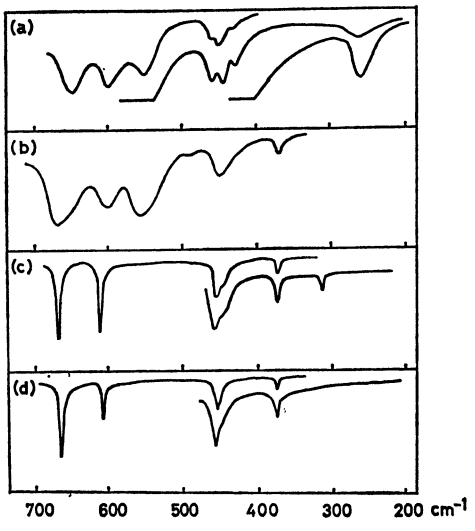


Fig. 1. Infrared spectra of 1,4-pentadiene.
(a) gas, (b) liquid, (c) glassy solid, (d) annealed solid.

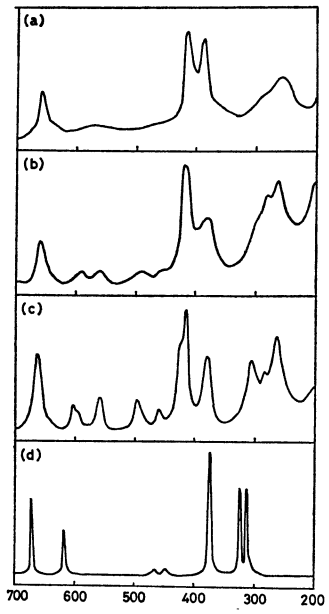


Fig. 2. Raman spectra of 1,4-pentadiene.
(a) gas (550 Torr), 296 K, (b) liquid, 273 K
(c) liquid, 163 K, (d) solid, 77 K.

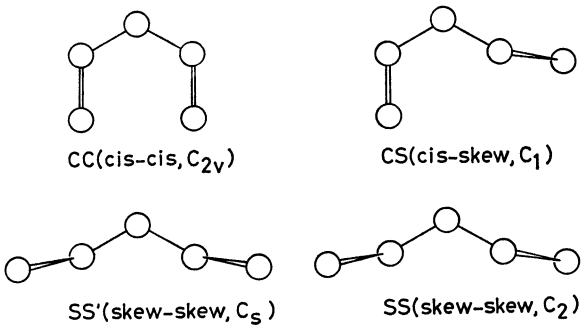


Fig. 3. Possible conformations of 1,4-pentadiene.

in the glassy state (Fig. 1c) which disappear in the spectrum in the crystalline state (Fig. 1d) are evidently assigned to another isomer. A third isomer is clearly identified by the bands at 555 and 268 $cm^{-1}$ newly appearing in the spectra in the gaseous and liquid states (Figs. 1a and 1b). Gallinella and Cadioli misassigned these two bands to two different isomers.[4]

*Normal Vibration Calculations.* Normal frequencies were calculated for the purpose of the assignment of the observed bands to the rotational isomers. For the calculation of normal frequencies and normal modes, a Hitachi 5020E computer at the Computer Centre of the University of Tokyo and the programs BGLZ and LSMB prepared in our laboratory were used.[5] The values of the bond lengths and angles were taken from the corresponding values of 1-butene and are listed in Table 1.[2] The torsion angles were assumed as 0° for the *cis* form and 120° for the skew form.

The wagging constants, the torsional constants, wagging-torsion interaction constants and the *cis* C· · ·C repulsive constant were introduced in addition to the simple Urey Bradley force field. The values of the

Table 1. Molecular parameters used in the normal vibration calculation

| | | |
|---|---|---|
| Bond lengths (Å) | | |
| C-C | 1.507 | |
| C=C | 1.336 | |
| C-H(methylene) | 1.095 | |
| C-H(vinyl) | 1.09 | |
| Bond angles | (a) | (b) |
| ∠CCC | 114.8° | 112.1° |
| ∠C=CC | 126.7° | 125.4° |
| ∠HC=C | 120.0° | 120.0° |
| ∠HC-C(vinyl) | 115.1° | 117.1° |
| ∠HCH(vinyl) | 120.0° | 120.0° |
| ∠HCH(methylene) | 105.2° | 105.7° |
| ∠HCC(methylene) | 109.1° | 109.6° |

(a) For the CC form. (b) For the CS, SS, and SS' forms.

Table 2. Force constants used in the normal vibration calculation[a)]

| | | | |
|---|---|---|---|
| Strtching (md/Å) | | | |
| K(=C-H) | 4.39 | | |
| K(C-H) | 4.23 | | |
| K(C=C*) | 7.42 | | |
| K(C-C*) | 3.24 | | |
| Bending (md/Å) | | Repulsive (md/Å) | |
| H(HCH) | 0.365 | F(HCH) | 0.21 |
| H(HC=C) | 0.16 | F(HC=C) | 0.45 |
| H(HC*C') | 0.21 | F(HC*C') | 0.38 |
| H(HC'H) | 0.37 | F(HC'H) | 0.21 |
| H(HC'C*) | 0.23 | F(HC'C*) | 0.51 |
| H(C=C*C') | 0.287 | F(C=C*C') | 0.40 |
| H(C*C'C*) | 0.26 | F(C*C'C*) | 0.40 |
| Wagging (md·Å) | | Torsion (md·Å) | |
| W(=$CH_2$) | 0.30 | Y(C=C*) | 0.485 |
| W(=CH) | 0.359 | Y(C'-C*) | 0.1 |
| Wagging-torsion interaction (md·Å) | | | |
| WT(CH wag, C=C tor) | 0.063 | | |
| Intramolecular tension (md·Å) | | | |
| $\kappa$ | 0.015 | | |
| *Cis* repulsive constant (md/Å) | | | |
| R(C†=C-C-C†)[b] | 0.169 | | |

a) C, C*, and C' are the carbons in =$CH_2$, =CH-, and -$CH_2$- parts of the molecule, $CH_2$=C*H-C'$H_2$-C*H=$CH_2$. b) Force constant between C†'s in the *cis* form.

force constants were transferred from those of olefins[3] and used without further modification (Table 2). The calculated frequencies below 700 $cm^{-1}$ are compared with the observed in Table 3 and Fig. 4. Assignments based on the potential energy distribution are also given in Table 3.

Shimanouchi, Abe, and Alaki showed that the CH out-of-plane vibration consisting of the C=C torsion and CH wagging modes is a good key band for the study of the rotational isomerism of 1-olefins.[3] When $CH_2$=CH-$CH_2$-C group takes the skew conformation, the CH out-of-plane vibration couples with the skeletal

Table 3. Observed and calculated frequencies of 1,4-pentadiene in $cm^{-1}$

| Observed | | | | | | | Calculated | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| gas | | liq. | | glass | solid | | | | | | |
| IR | R | IR | R | IR | IR | R | C-C | C-S | S-S′ | S-S | P. E. D. (%) |
| 650 | 662 | 666 | 665 | 664 | 664 | 672 | | | | 643 | CH wag(36) C=C tor(22) CCC def(9) |
| | | | | | | | 642 | | | | C=CC def(41) CCC def(28) $=CH_2$ rock(22) |
| | | | | | | | | | 637 | | CH wag(30) C=C tor(25) CCC def(7) |
| 590 | | 600 | 604 | 610 | 610 | 618 | | | | 609 | CH wag(49) C=C tor(25) |
| | | | 597 | | | | | | 605 | | CH wag(55) C=C tor(25) |
| | | | | | | | | 603 | | | CH wag(20) C=C tor(20) CCC def(19) |
| 555 | 580[a] | 555 | 560 | | | | | 585 | | | CH wag(46) C=C tor(16) |
| | | | | | | | 550 | | | | CH wag(61) C=C tor(43) |
| | | | | | | | 522 | | | | CH wag(61) C=C tor(28) |
| | 475[a] | | 494 | | | | | 486 | | | C=CC def(34) CH wag(29) C=C tor(22) |
| 457 | | 450 | 457 | 455 | 455 | 457 | | | | 470 | C=CC def(77) |
| 446 | | | | 444 | | | | | 437 | | C=CC def(89) |
| 425 | | | 421 | | | | | 425 | | | C=CC def(76) |
| | 415 | | 418 | | | | | | 419 | | C=CC def(56) |
| | | | | | | | 412 | | | | CCC def(68) |
| | 387 | 370 | 380 | 375 | 375 | 376 | | | | 367 | C=CC def(67) |
| | | | 305 | | | 318 | | | | 325 | CCC def(57) C=CC def(14) |
| | | | 285 | 306 | | | | | 310 | | CCC def(62) C=CC def(17) |
| 268 | 260[b] | | 265 | | | | | 264 | | | CCC def(34) C=CC def(19) |
| | | | | | | | 226 | | | | C-C tor(92) |
| | | | | | | | 206 | | | | C=CC def(30) CCC def(30) |

a) Weak broad band. b) Broad band.

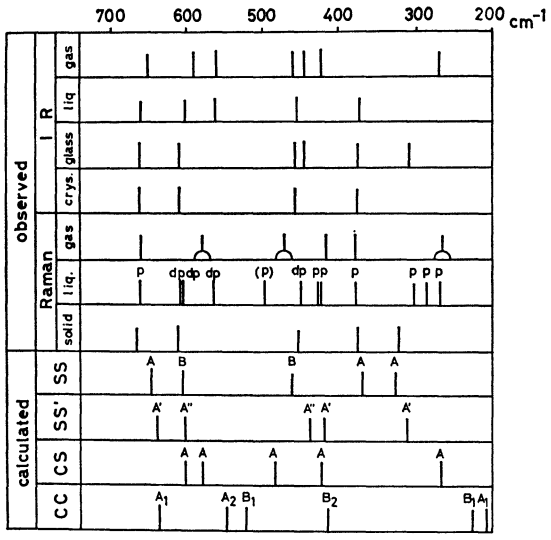


Fig. 4. Observed and calculated frequency patterns of 1,4-pentadiene.

deformation vibrations and gives a frequency near 640 $cm^{-1}$, while this coupling does not occur for the *cis* conformation the former giving a frequency near 580 $cm^{-1}$. There are two such vibrations for each isomer in the case of 1,4-pentadiene. These vibrations of the CC form do not couple with the skeletal deformation by symmetry requirement and give frequencies, 550 and 522 $cm^{-1}$. For the SS and SS′ forms, the symmetric CH out-of-plane vibration couples with C–C–C deformation and gives a frequency near 640 $cm^{-1}$ and the antisymmetric CH out-of-plane vibration gives a frequency of about 610 $cm^{-1}$. The skew and *cis* parts of the CS form have the frequencies 603 and 585 $cm^{-1}$, respectively. Therefore, the frequency of the CH out-of-plane vibration can also be a clue to the assignment of rotational isomers in the case of 1,4-pentadiene. The difference in frequency of C–C–C deformations may be useful for the discrimination of the SS form from the SS′ form.

*Stable Conformations.* From the results given in Table 3 and Fig. 4, it can be concluded that the conformation in the crystalline state is the SS form. The frequencies calculated for this form are 643, 609, 470, 367, and 325 $cm^{-1}$. They correspond to the five Raman lines at 672, 618, 457, 376, and 318 $cm^{-1}$. The calculated values for the CC and CS forms differ greatly from the observed in the crystalline state. There is a possibility that the SS′ form exists in the crystalline state. However, it is not probable since the frequencies 437 and 419 $cm^{-1}$ calculated for the SS′ form do not correspond to the observed.

The appearance of two frequencies at 444 and 306 $cm^{-1}$ in the spectrum of glassy state in addition to the bands observed in the crystalline state is explained by the coexistence of the SS and SS′ forms. These two bands are assigned to the calculated frequencies, 437 and 310 $cm^{-1}$, of the SS′ form. Moreover, the change of the relative intensities of the infrared bands at 664 and 610 $cm^{-1}$ on going from the crystalline state to the glassy state can be explained by the overlap of the two CH out-of-plane vibrations of the SS′ form with those of the SS form. Thus, the third isomer corresponds to the CS form. Actually, the Raman lines (infrared bands) at 560 (555), 494, ~420 (425),

and 265 (268) $cm^{-1}$ are in good agreement with the frequencies calculated for the CS form, 585, 486, 425, and 264 $cm^{-1}$. No corresponding bands to the calculated frequencies of the CC form were found in the spectra.

Now, the stable isomers of 1,4-pentadiene are proved to be the SS, SS′, and CS forms. It is noteworthy that these forms are in accord with those of the stable isomers predicted by *ab initio* MO calculations.[4] It is to be noted that the band broadening and the frequency shifts are distinctly observed by the change in the temperature in the liquid state. This tendency is also observed in the spectrum in the gaseous state. The spectral changes are far more pronounced than in the case of 1,2-dichloroethane[6] and other molecules[7] with the usual C–C torsion axis. This suggests that the barrier to internal rotation is low except for the *cis-cis* barrier and the anharmonicity in the potential function causes the band broadening and frequency shifts.

## Conclusion

It is shown that 1,4-pentadiene exists in the SS form in the crystalline state. The SS and SS′ forms coexist in the glassy state while three forms, the SS, SS′, and CS, are found in the liquid and gaseous states. Although the intensities of the Raman lines at 560 and 494 $cm^{-1}$ decreased slightly and the line at 305 $cm^{-1}$ broadened and shifted toward lower frequency at a higher temperature (Figs. 2b and 2c), no significant intensity change due to the temperature change was observed. This shows that the energy difference among the three isomers is not very large and the stability of the SS form in the crystal can be ascribed to the possible close packing of the molecules.

## References

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